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IRON OXIDE IN ENAMEL GLASS AS DISSOLVED FROM THE METAL BASE*

By Andrew I. Andrews and Howard R. Swift

Abstract

The iron oxide content of an enamel glass was measured by the use of a predetermined curve representing iron oxide versus the index of refraction. It was found that the iron oxide content of the glass adjoining the interface between the enamel and the iron base rises sharply in the early stages of firing to a value close to the solubility limit of the glass after which it gradually falls to a constant value. The iron content at the surface remains low until that at the interface decreases, whereupon the surface concentration correspondingly increases. The cobalt additions resulted in a lower iron content in solution at the interface, but they increased the dendrite content of the glass. A decrease in the cobalt content resulted in an opposite effect. There was a direct relation between the amounts of cobalt and dendrites and the adherence. The effects of temperature and thickness of application are given, and the results are discussed.

I. Introduction

Although there have been extensive investigations of the phenomena related to the adherence of sheet-iron, ground-coat enamels, the data concerning the solution of iron oxide during firing have been meager. Because the solution of iron oxide by the enamel appeared to be related to the general phenomena of adherence, an investigation was undertaken to determine the amount and distribution of iron oxide in cobalt ground-coat enamels at different stages of firing.

II. Procedure

Gilard and Dubrul[1] report a practically linear increase in the index of refraction of soda-lime-silica glasses with additions of iron oxide. Dietzel and Meures[2] determined the increase of the index of refraction of a glass for a 1% increase in iron oxide, and they obtained an extrapolated curve from these data to determine the amount of iron oxide concentration in enamel coating, but their results were unreasonably high.

The present writers thought that the index of refraction could be used as a quantitative means of measuring the iron content of an enamel glass by determining the curve for the index of refraction versus the iron oxide content and by measuring the index for the enamel glass; the iron content then could be determined directly from the curve.

The preliminary part of the present investigation consisted of adding 5, 10, 12.5, 15, 17.5, 20, 22.5, 25, and 30 parts by weight of ferric oxide to 100 parts of glass batch of the following composition, which is an average used in sheet-iron ground coats:

	(%)		(%)
Feldspar	30	Soda niter	5
Borax	30	Fluorspar	6
Quartz	20	Cobalt oxide	0.5
Soda ash	7	Manganese dioxide	1.5

The batches containing the iron oxide were smelted at 2100°F. and quenched in water. The index of refraction was determined for each of these frits by the central illumination method. A series of oils made with alpha-monochloronaphthalene and medium government oil was standardized to the sodium line with an Abbé refractometer at 20°C. and 30°C. An electrically heated stage on the microscope facilitated the most accurate work so that, by using the single-variation method suggested by Emmons[3] and a maximum

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Enamel Division). Received April 14, 1941; revised copy received November 27, 1941.

This paper was prepared from a thesis written by the junior author to satisfy in part the requirements for the degree of Bachelor of Science in Ceramics at the University of Illinois.

[1] P. Gilard and L. Dubrul, "Calculation of Physical Properties of Glass: III, Index of Refraction," *Jour. Soc. Glass Tech.*, **21** [88] 485–88 (1937); *Ceram. Abs.*, **17** [9] 301 (1938).

[2] A. Dietzel and K. Meures, "Reactions Important for Adherence When Firing Ground Coats Containing No Adhering-Promoting Oxides," *Jour. Amer. Ceram. Soc.*, **18** [2] 35–37 (1935).

[3] R. C. Emmons, "Double-Dispersion Method of Mineral Determination," *Amer. Mineralogist*, **13** [10] 504–15 (1928); *Ceram. Abs.*, **8** [1] 70 (1929).

temperature variation of 0.15°C., the error in the indices was reduced to 0.001.

The effect of the varying iron content on the index of refraction of the glasses was practically linear as shown in Fig. 1. There are no breaks, changes in curvature, or points not falling on the curve except at the higher values where the glass becomes saturated with iron oxide. Crystals of iron oxide were precipitated from melts (*a*), (*b*), and (*c*), which accounts for the erratic results obtained with these compositions. Melts (*a*) and (*c*) were identical in composition. Melt (*c*), however, was cooled slowly instead of being quenched, and it obviously shows that much more iron oxide crystallized out of solution. This decrease in iron oxide accounts for the decrease in the index of refraction of the glassy portion which was deficient in iron oxide.

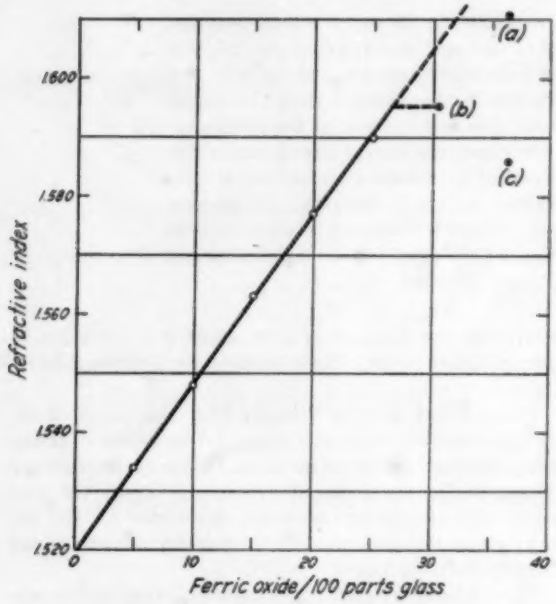

FIG. 1.—Effect of ferric oxide on index of refraction.

The major part of this research consisted of studying the fired enamel glass at certain points such as those at the interface with the iron and near the air-glass surface. The solubility limit of the glass was determined, and the dendrite formation was closely observed. It was soon found that the index of the glass at the interface was high and that it tended to decrease toward the surface of the enamel. Specimens were therefore selected for measurement, some with a maximum index at the interface and others with a minimum index at the surface of the enamel. This selection eliminated the necessity of knowing the accurate position of a particular chip of enamel being studied.

To obtain the specimens at the interface, the enamel was broken and, under a binocular microscope, small pieces were gouged off the iron with a sharp point. The specimens were transferred to a microscope slide with a drop of suitable oil, a cover glass was placed over the drop, and the slide was examined under a magnification of 360 times. The results were considered to be accurate only if the index was the highest of any chip, excluding those chips occurring from copperheads, slag spots, or burnt edges. A good grain, in general, was light green in color and showed a multitude of fine particles which appeared to be dendrites. The yellow line of sodium was always used to obtain the index as this line was used in the calibration of the oils. The enamel at the surface of the coating was studied in a similar manner except that only the lowest index grains were used.

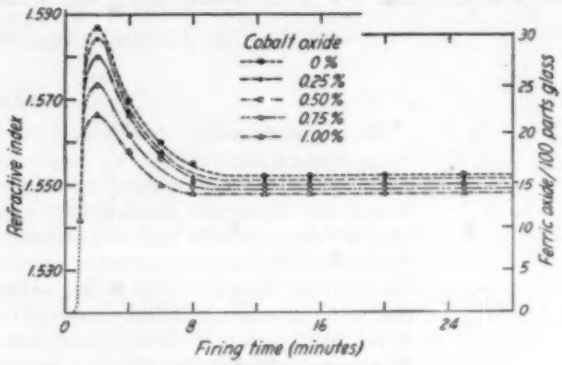

FIG. 2.—Effect of cobalt content on amount of iron in solution at the interface as affected by firing time.

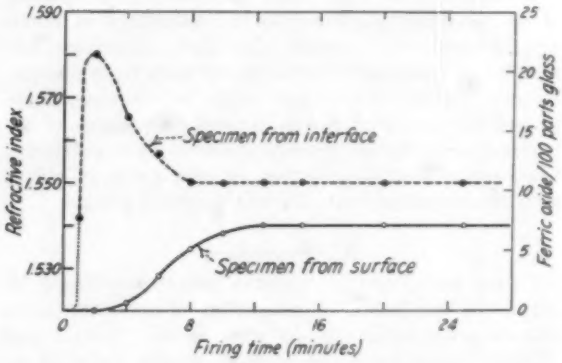

FIG. 3.—Comparison of the iron oxide content at the interface and surface.

The solubility limit was obtained by using scaled pieces to which enamel was evenly applied. The resultant pieces were masses of copperheads surrounded by dark green glass. The indices were obtained by the standard central illumination method for chips which were obtained as close as possible to a copperhead. The hematite flakes were disregarded in obtaining the index. Owing to the profusion of foreign material present in the glass samples, these determinations were difficult to make.

The solubility limit of the glass at 1600°F. as measured by the index of refraction was 24.5% by weight;

this value agrees with the results of Spencer-Strong and King,[4] which were obtained under different conditions. The variation of cobalt between 0% and 1.0% did not appreciably affect this limit.

III. Variables Influencing Results

Inasmuch as the iron content was determined by comparing the changes in the index of refraction and by using this as a measurement of the iron content, the variables influencing these results were studied. Some of the specimens were sprayed with enamel on one side and others on both sides to determine whether or not this factor affected the iron content; some were cleanly pickled, whereas others were rusted slightly to note the effect of pickling. Samples of the enamel glass, which were not in contact with the iron, were fired for varying lengths of time to determine the effect of the heat-treatment on the results. Samples which had a heavy application at one end grading to a very thin application at the other end were also examined to note the effect of variable thicknesses. The first factors, namely, the pickling process, the application of enamel to one or both sides, and the heat-treatment, were of minor importance only as far as the maximum index at the interface was concerned, but the variations in thickness showed a marked affect on the results.

The effect of ferrous oxide on the original curve, iron content versus index of refraction, was studied by introducing sugar in the batches as a reducing agent and by smelting them in a gas-fired muffle furnace under reducing conditions. The change in index, which was 0.002, was quite small for the high percentage of iron oxide. It was therefore concluded that the presence of ferrous iron is capable of changing the results but that the effect of this slight change is negligible.

IV. Results

The effect of cobalt on the solution of iron oxide is shown in Fig. 2. These data represent the iron content at the interface as determined by measuring the index of refraction. The curves show that there is a maximum in iron content at the interface in about 2 minutes of firing but that it then drops rather sharply to a constant value. Good adherence was not obtained for these samples until the peak was reached. The enamels with no cobalt had poor adherence, and those with a higher cobalt content had excellent adherence. There was, moreover, little decrease in the adherence even after some of the samples were fired for 60 minutes. These long-fired samples were also free of copperheads, and they did not burn off so much as might be expected. The minimum iron content at the surface rose correspondingly, as the maximum dropped, to a value somewhat lower than that at the interface, maintaining a slight index gradient (see Fig. 3).

Figure 4 shows the effect of temperature on the rate of solution of the iron oxide. The amount of iron in solution at the peak of the curve was about the same in all cases, but a longer time was required to reach the maximum iron content with a lower temperature. The rate of decrease of the iron content with longer firing time is not so great at the lower temperatures as it is at the higher, and the curves tend to level off somewhat faster at the lower temperatures.

Figure 5 shows the effect of enamel thickness on the rate of solution of iron oxide. These data were obtained at the interface. The thicker applications contained less iron in solution after the peak was reached, and the rate of decrease of the iron content was more rapid with the thicker applications.

In the enamels containing no cobalt, very few dendrites were present, whereas the dendrites increased in those which contained cobalt. Two types of dendrites seemed to be present, namely, (*a*) those high in the glass

[4] G. H. Spencer-Strong and R. M. King, "Mechanics of Enamel Adherence: IX, Equilibrium Studies of Some Systems of Enamel Glass and Cobalt, Nickel, and Iron Oxides," *Jour. Amer. Ceram. Soc.*, **17** [7] 208–14 (1934).

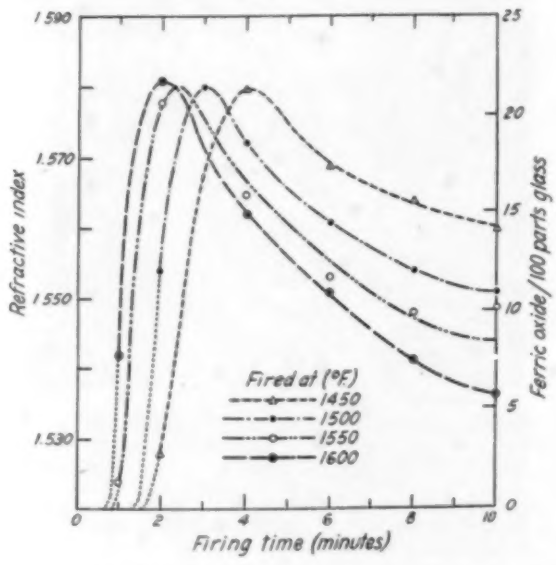

FIG. 4.—Effect of firing temperature on amount of iron oxide in solution at the interface as affected by firing time.

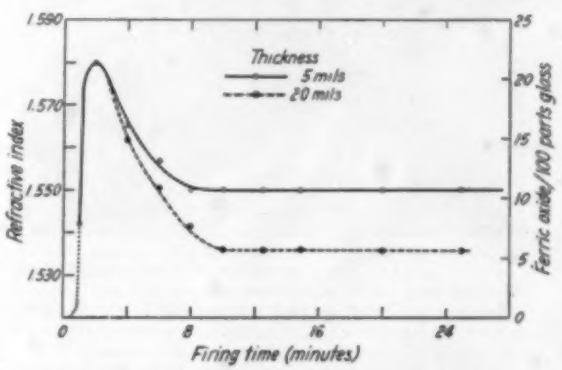

FIG. 5.—Effect of thickness on the concentration of iron oxide at the interface as affected by firing time.

away from the iron, termed secondary dendrites, and (*b*) those at the interface, called primary dendrites. The adherence was quite poor until the 2-minute firing stage was reached when the dendrites developed and the primary scale apparently dissolved.

Figures 6 and 7 show the effect of firing time on the development of the dendritic structure, and Figs. 8 and 9 and Fig. 7 (*A*) show the effect of the cobalt content of the enamel on the development of the dendrites. It was not possible to secure typical specimens of the entire field although an attempt was made to do so. All of the photomicrographs are at a magnification of 350 times.

V. Discussion of Results

(1) Sources of Error in Data

Because this method of obtaining the iron content of an enamel glass is relatively unusual, the sources of error will be discussed in detail. The three general types of error are those resulting from the preparation of the test pieces, those from actual measurements on the pieces, and those inherent in the method.

The errors resulting from the preparation of the test pieces are insignificant. The curves which show the index of refraction versus the firing time for the varying thicknesses and temperatures indicate that quite large fluctuations will have little effect on the results. The slight variations which might occur in the preparation of the test pieces would therefore have little affect on the results. Because numerous grains from different parts of the pieces were examined, the effect of these errors may be minimized.

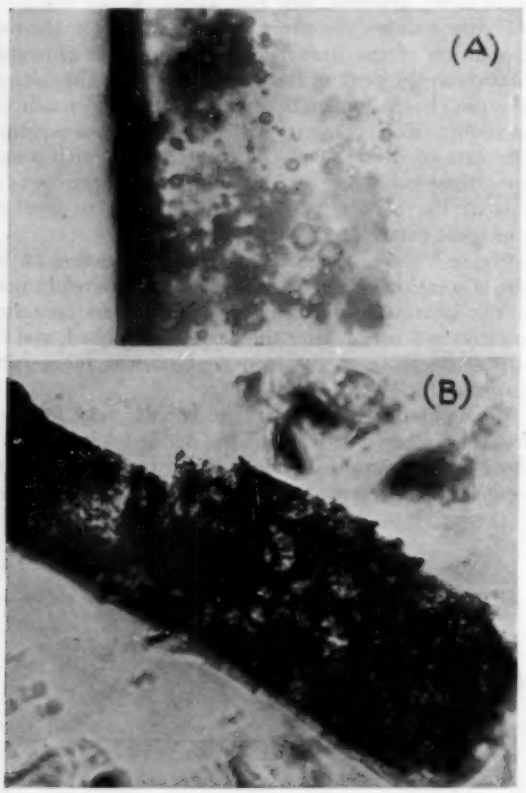

FIG. 6.—(*A*) Chip almost perpendicular to surface of metal and therefore a cross section of glass; no adherence and index quite low showing little iron had gone into solution; 1% of cobalt oxide; fired 1 minute at 1600°F.

(*B*) Grain taken at slight angle to surface; slight adherence and some iron had gone into solution; 1% of cobalt oxide; fired 1½ minutes at 1600°F.

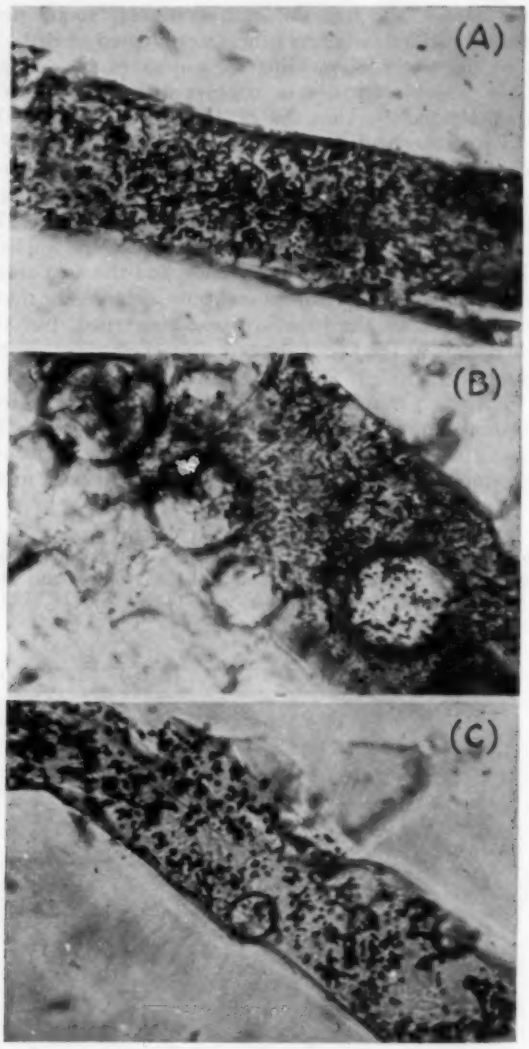

FIG. 7.—(*A*) Chip probably taken almost parallel to surface; black spots are dendrites of magnetic material; excellent adherence; 1% of cobalt oxide; fired 2 minutes at 1600°F.

(*B*) Fewer dendrites than chip in Fig. 7 (*A*), possibly due to selection of the grain; good adherence; 1% of cobalt oxide; fired 8 minutes at 1600°F.

(*C*) Abundance of dendrites but not quite so many as in Fig. 7 (*A*); they are slightly larger, but this may be due to selection of the grain; excellent adherence; 1% of cobalt oxide; fired 15 minutes at 1600°F.

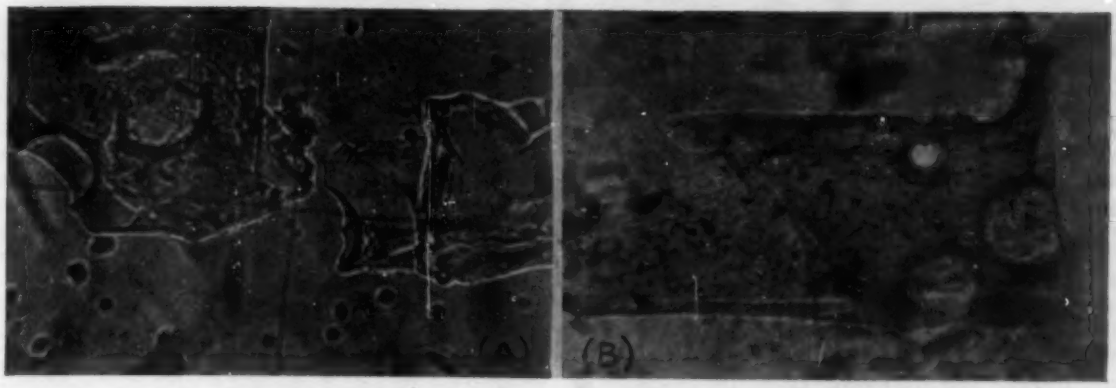

FIG. 8.—(*A*) Uniform light greenish glass; very few, if any, dendrites; no adherence; 0% of cobalt oxide; fired 2 minutes at 1600°F.
(*B*) Adherence quite poor (photomicrograph overexposed to bring out dendrites more clearly); 0.25% of cobalt oxide; fired 2 minutes at 1600°F.

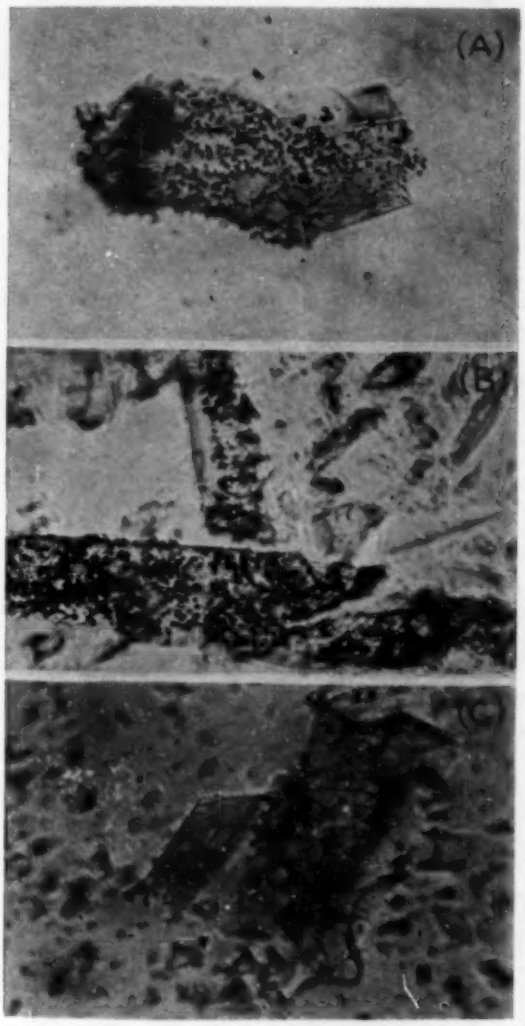

FIG. 9.—(*A*) Chip almost parallel with metal; lower end slightly closer to metal; good adherence; less iron in solution but more present as dendrites than in sample shown in Fig. 8 (*B*); 0.5% of cobalt oxide; fired 2 minutes at 1600°F.
(*B*) Dendritic structure plainly seen; excellent adherence; 0.75% of cobalt oxide; fired 2 minutes at 1600°F.
(*C*) Identical with sample shown in Fig. 9 (*B*), except that the chip was obtained higher from interface; there is more development of secondary dendrites; 0.75% of cobalt oxide; fired 2 minutes at 1600°F.

Another source of error occurs from the measurements of the indices of refraction. The immersion method is generally conceded to be accurate within 0.003. Inasmuch as a large set of oils was checked at the beginning of the investigation and a temperature control was used, this error was probably reduced to 0.002. The dispersion was practically a constant for this glass, and as the same type of material was always examined, the estimation was facilitated. The stresses occurring in the glass also changed the index of refraction, but the selection of minute pieces of glass nullified this error. Several determinations were made on each sample, using the same size of chips of the same general appearance, which eliminated errors due to small copperheads, slag spots, or other such high index spots.

There may be minor errors inherent in the method. It has been assumed (*a*) that changes in the index of refraction of glass occur only when the amount of iron oxide is increased or decreased and (*b*) that the iron is in the higher valence state. The first assumption has been shown to be correct, but the second undoubtedly may introduce a small error, owing to the presence of ferrous oxide as well as of ferric oxide. This ratio probably keeps changing with the firing time. The ferrous glass showed a slightly higher index than the corresponding ferric oxide glass, but this change was practically insignificant.

(2) Analysis of Data

When the maximum index or iron content at the interface is plotted against the firing time, the curves tend to rise to a peak quite rapidly and then to drop to a

constant value (see Figs. 2, 3, and 4). The minimum index at the surface remains low until that at the interface falls, whereupon it rises to a corresponding degree. There are essentially three parts to the curve showing the iron content at the interface versus the time, namely, (*a*) the part where the iron content is practically zero in the early stages of firing, (*b*) that where the iron content increases rapidly to the maximum, and (*c*) that where the iron content falls to a nearly constant value. The stages of firing deduced from (1) an examination of the photomicrographs, (2) the observations of pieces in the different stages of firing, and (3) an analysis of the rate of iron solution curves are described. In (*a*), the metal and the enamel are heated with a coating of scale forming over the metal; in (*b*), the enamel glass fuses shutting off the oxygen supply, the scale goes into solution, and, at the same time, a dendritic formation and adherence develops; and in (*c*), the iron concentration is lowered by a diffusion toward the surface of the iron oxide, thus decreasing the actual concentration at the interface but increasing that at the surface.

The thicker enamels tend to reach a lower final equilibrium concentration because there is more glass present to dilute the iron oxide. The rate of diffusion of the iron in stage (3) is greater because of the larger volume. Cobalt lowers the amount of iron in solution at the interface but raises the dendrite content of the glass. It is reasonable to infer from the curves in Fig. 2 that the same total amount of iron (in the form of the oxide and possibly alpha-iron) is actually in each glass sample, in which the cobalt content was varied, after fusion of the glass had taken place because practically the same equilibrium value was reached in all cases. The slight lowering of the amount in solution when cobalt was added is due to the formation of dendrites.

Because the slight lowering of the temperature probably does not affect the amount of scale formed very much, it is not surprising that the same maximum would be reached in stage (*b*) for the various firing temperatures. The lower firing temperature permits a longer period for the formation of scale, whereas the higher temperature evidently produces a similar scale in less time. The diffusion after the maximum concentration was reached was not so rapid at the lower as at the higher temperatures, a fact which would be expected from the viscosity-temperature relationships.

VI. Summary

The results obtained in this investigation show that a measure of the index of refraction of glass is a quantitative means for determining the amount of iron oxide in solution in ground-coat enamel coatings. This is particularly true inasmuch as the results are not appreciably affected by the degree of oxidation of the iron oxide or by the heat-treatment of the glass.

Additional results may be summarized as follows:

(1) The solubility limit of iron oxide is never reached in ground coats, normally applied and uniformly fired, even after firing 60 minutes.

(2) The primary scale which forms in the first two minutes of firing is the major source of iron oxide in the enamel.

(3) There is evidence that the degree of adherence may be directly correlated with the amount of dendrite formation.

(4) The effect of cobalt additions up to 1% is to increase the dendrite content.

(5) For the particular composition studied, additions of cobalt decrease the amount of iron in solution, especially in the earlier stages of firing.

(6) The solubility limit is not affected by minor additions (up to 1%) of cobalt.

(7) A lowering of the firing temperature delays the solution of the iron oxide and retards the diffusion of the oxide although the iron content is not changed appreciably.

(8) An increase in the thickness of application gives the same amount of iron in solution before diffusion takes place, but there is also a lower final concentration of the iron oxide.

(9) The iron content at the surface of the enamel remains low until diffusion from the interface occurs; it then rises to a value somewhat lower than that of the interface.

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PLASTICITY OF CLAYS*

By E. A. Hauser and A. L. Johnson†

Abstract

A theoretical discussion is presented on the plasticity of clays from a colloid-physical standpoint and based on modern concepts of the nature and source of the charges associated with the colloidal system.

I. Introduction

The term "clay" as used herein refers to a group of hydrous, crystalline aluminum- or magnesium-silicates which are characterized by (*a*) a typical layer or sheet lattice,[1] (*b*) plastic properties, and (*c*) very fine particle size. These silicates have been the object of extensive study by many technologists. Although approximately twelve distinct minerals make up this clay-mineral group, only a few occur in nature in such abundance as to make their commercial application of economic interest. Of these minerals, kaolinite and bentonite‡ probably have the most general use because of their elastico-plastic properties. An "elastico-plastic solid" may be defined as one which obeys the laws of an elastic solid for shearing stress values below the critical stress (corresponding to the elastic limit in shear) and which deforms plastically when the shearing stress exceeds the critical value. The yield point of a freshly molded clay piece is important in relation to its use in handling. Ware which has been prepared from slips exhibiting high yield values may be moved safely and without any distortion. Gravity may be another factor causing the deformation or slump of the ware while it is standing.

The success of the forming operation, wherein the clay is sheared by the jigger tool, depends on the extensibility of the clay. If the extensibility is low, cracking and tearing of the ware will occur during the forming operation unless careful adjustments are made of the speed of the revolving clay mass.

The present discussion evaluates the importance of these factors and their relation to the colloidal aspects of a clay–water system. The mineral, kaolinite, is specifically considered herein, and the theoretical reasoning applies directly to this mineral unless otherwise stated. (The bentonites are referred to only in section IV.)

Kaolinite is composed of a hydrated silica sheet and a gibbsite sheet, the two joined together by oxygen bridges which result from the condensation of OH groups when the two layers are stacked on each other.[1] A crystal of the layer lattice type occurs, which is electrically neutral except for spots of unsaturation along the edges of the sheets.

Montmorillonite as chief constituent of bentonitic rocks is composed in its ideal form of two hydrated silica sheets with their vertex OH groups pointing toward each other and a gibbsite sheet sandwiched between them. The three sheets are united by the same condensation mechanism previously mentioned. Such an ideal structure, however, is rarely found in nature. Partial substitutions of aluminum by magnesium in the gibbsite sheet and of silicon by aluminum in the silica sheets are frequent, and a particle with an unbalanced lattice results in both cases. The montmorillonite particle then carries a net negative charge on its surface.

A study of the flow characteristics of a kaolinite–water system over a more or less complete range of concentration of kaolinite shows that at extreme dilutions (less than 1%) the system behaves as a true liquid, that is, it exhibits truly viscous flow. A transition from this viscous flow to elastico-plastic flow occurs only at higher concentrations of clay. This change in the flow characteristics of a kaolinite–water system has not yet been investigated in great detail. The real causes for the existence of elastico-plastic flow or the yield value in this or similar systems, therefore, have not been satisfactorily determined.

In kaolinite or in any other of the clay minerals, the particle-size distribution, particle shape, and total surface area and their effect on the close packing of the system as well as the presence of organic material result in variables, which undoubtedly affect the flow properties of this system and which may well account for certain anomalies encountered. Thus far, the ions associated with the colloidal particles have been overlooked. They introduce new, important, and heretofore neglected characteristics. A recognition of the influence which these ions exert is therefore necessary before the results obtained from the study of flow properties can be helpful in accounting for the other properties of the system; in other words, the colloidal nature of the entire system must be considered.

The subject matter of plasticity, therefore, will be presented strictly from the viewpoint of recent developments on the colloidal nature and properties of kaolinite and of the kaolinite–water systems.

II. Plasticity of Kaolinite Slips from a Colloidal Viewpoint

The significant difference between a system which exhibits truly viscous flow and one which exhibits

* Presented at the Annual Meeting of the Society of Rheology, October 24–25, New York City, 1941. Received November 8, 1941.

† The authors are associated, respectively, in the Department of Chemical Engineering and the Division of Ceramics, Massachusetts Institute of Technology, Cambridge, Mass.

[1] E. A. Hauser, "Colloid Chemistry in Ceramics," *Jour. Amer. Ceram. Soc.*, **24** [6] 179–89 (1941).

‡ The term "bentonite" refers to a rock formation, the major constituents of which are members of the montmorillonite class of clay minerals (see footnote 1).

truly plastic flow is the initial expenditure of force before the occurrence of shear in the latter system; some force exerting its influence in a plastic system must first be overcome before the proportional relationship of applied force to shear, which is characteristic of a truly viscous system, can apply. The point at which this relationship is finally achieved is called the "yield point" and, by definition, it constitutes a measure of plasticity. Plasticity in clay systems is the result of the attraction and repulsion forces set up between the colloidal clay particles and the ions in the dispersion medium. A discussion of these forces follows.

The forces of attraction associated with a colloidal micelle arise from one of the following conditions[2]: (1) The colloidal particle, owing to an unbalanced lattice structure, carries a net surface charge; (2) the particle acquires a net surface charge as a result of the preferential adsorption of ions from the dispersion medium; or (3) the particle dissociates ions from its surface into the dispersion medium and thereby becomes charged.

In the specific case of kaolinite, hydroxyl ions may be preferentially adsorbed.[3] The kaolinite particle, consequently, takes on a net negative charge, and an attraction is set up between the kaolinite particle and any positive charges in its vicinity. The repulsion forces that are associated with the colloidal micelle[2] originate with the counterions which swarm about the colloidal particle in an effort to neutralize its surface charge. These counterions complete the diffuse double layer, and, although they may be any cation, the amount of repulsive force existing in the system depends on the type of cation serving as the counterion.[3] With this general picture established, it is possible to present a more detailed discussion of the forces associated with the colloidal micelle in the kaolinite–water system.

A kaolinite particle in a water medium is first considered in which the counterions are any of the monovalent alkali metals such as sodium. Figure 1 shows the arrangement of the adsorbed hydroxyl ions and the counterions as well as the relationship of the attraction and repulsion forces which are present as a function of the distance from the particle. The broken circle represents the edge of the hypothetical, diffuse lyosphere or water hull associated with the colloidal particle. This water hull, taken to be an inherent part of the colloidal micelle, owes its existence either to (*a*) the hydration of the hydroxyl ions, which are firmly adsorbed on the surface of the kaolinite particle, or to (*b*) a dipolar orientation of water molecules on the particle surface.[4] Point d_1 represents the average distance from which all of the ions of the diffuse double

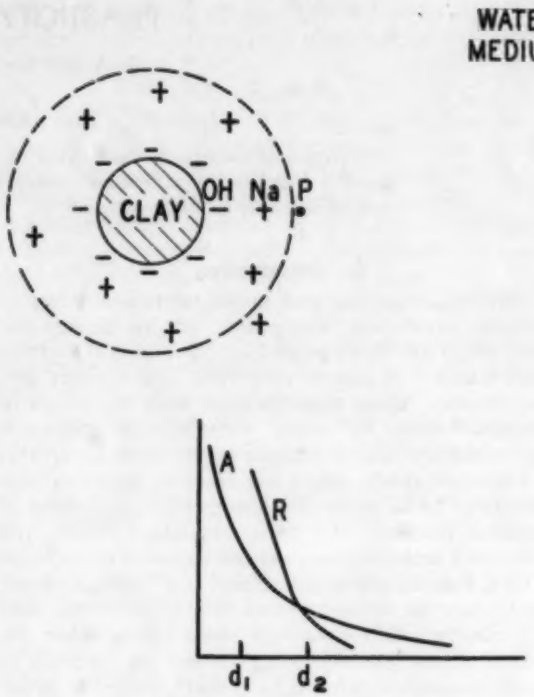

FIG. 1. Arrangement of ions associated with the clay OH–Na system and the relationship of the forces present in a watery medium (schematic).

layer, that is, the sodium countercharges, may be considered to act. Inasmuch as the dispersion medium is pure water in this ideal case, point *P*, where the charge that is associated with the colloidal micelle approaches zero, will lie in the vicinity of the hypothetical edge of the water hull or immediately outside it. The repulsive force resulting from the sodium counterions thus rapidly decreases at this distance, curve *R*. Curve *A*, which represents the attraction forces between the colloidal particle and the oppositely charged ions in the medium, shows that although the forces of attraction are weak they are still present at considerable distances from the particle. Thus, if kaolinite (in the clay OH-Na form) is dispersed in pure water, a slight attraction force exists at the edge of the water hull, which would be sufficient to cause two or more particles to flocculate.

If a small trace of an electrolyte (NaOH) is added to this system, profound changes in the forces connected with the micelle will occur as a result of the preferential ion adsorption on the particle and of the rearrangement of countercharges. Figure 2 shows such an arrangement of the ions of the system and of its attraction-repulsion forces as a function of distance. A considerable repulsion force exists at the edge of the lyosphere,[3] that is, the charge density on the particle and its potential is high, and the entire system is at maximum stability from a colloidal viewpoint because of the presence of large repulsive forces between particles. A kaolinite slip in this state is said to be deflocculated or dispersed, and it is used in this condition

[2] E. A. Hauser and S. Hirshon, "Behavior of Colloidal Suspensions with Electrolytes," *Jour. Phys. Chem.*, **43** [8] 1015 (1939); *Ceram. Abs.*, **19** [6] 146 (1940).

[3] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay, II," *Jour. Amer. Ceram. Soc.*, **24** [6] 189–203 (1941).

[4] S. B. Hendricks and M. E. Jefferson, "Structure of Kaolin and Talc-Pyrophyllite Hydrates, Bearing on Water Sorption of Clays," *Amer. Mineralogist*, **23** [12] 863–75 (1938); *Ceram. Abs.*, **18** [4] 113 (1939).

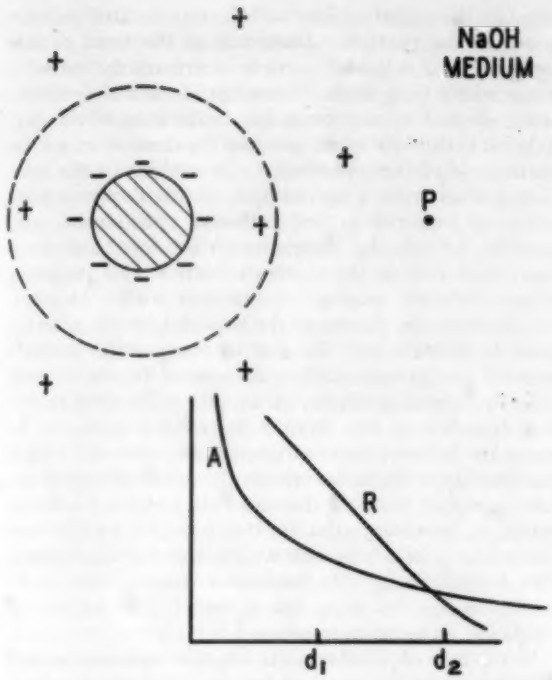

FIG. 2. Arrangement of ions associated with the clay OH–Na system and the forces present in an alkaline medium (schematic).

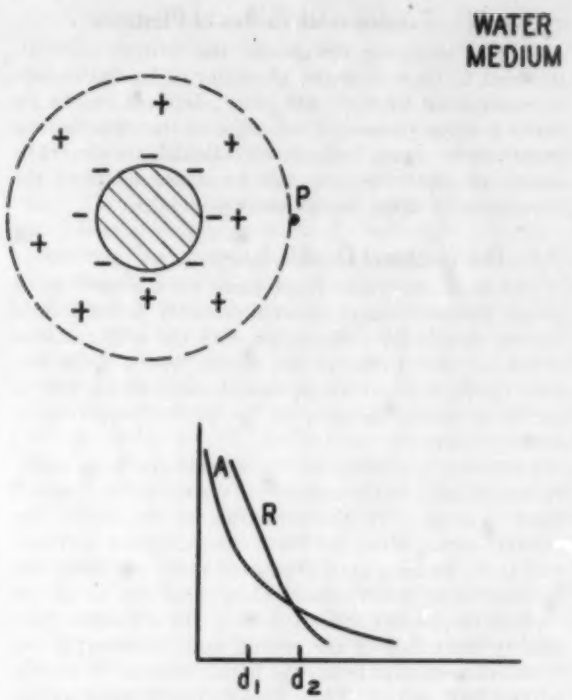

FIG. 3. Arrangement of the ions associated with the clay OH–H system and the forces present in a watery medium.

in the ceramic industry for commercial casting processes. These casting slips (sols) contain solids as high as 75 to 80% by weight. The flow properties of such a system, however, need further careful consideration, and they will be discussed after a consideration of the effect of the type of countercharges which occur in the kaolinite micelle.

A systematic study of the effect of the type of cation which acts as the counterion of a kaolinite micelle shows that, following the Hofmeister or lyotropic series from the alkali metals through the di- and tri-valent cations to the hydrogen, the net charge on the particle or the repulsion forces at the edge of the lyosphere steadily decrease in the same order because of the increased valency and lower degree of hydration of the cation. The distribution of the charges and the forces associated with a system containing kaolinite in the clay OH-H form in a pure water medium may be represented by Fig. 3.

Because of the positions which the hydrogen counterions take, all of the countercharges occur within the hypothetical water hull, and the discharge of the hydroxyl ions occurs. The repulsion forces, consequently, do not exist beyond the lyosphere. From a colloidal viewpoint, therefore, the system is unstable or flocculated.

Inasmuch as the attraction forces tend to agglomerate all particles, an initial expenditure of force is obviously needed to overcome the attraction forces inherent in such an agglomerated system before shear can occur. This input of force without resulting shear (yield point) is a characteristic of plastic flow. In view of this discussion, the kaolinite in the clay OH-H form in a pure water medium would result in establishing a maximum attraction force at the edge of the lyosphere, and this force would decrease in value in the progression from hydrogen to sodium in the lyotropic series of cations. Because the yield point would decrease with decreasing attraction forces or increasing repulsion forces, a kaolinite system containing clay OH-Na particles in a pure water medium theoretically would be the least plastic. The kaolinite in the clay OH-H form, by inference, should be the form exhibiting the highest yield point. (The effect of the concentration of solids in the system is discussed in section III (3).) The formation of a clay OH-Na particle in a pure water medium, however, is actually a theoretical state, and, practically, the excess electrolyte would have to be present in the system to insure the formation of clay OH-Na. The repulsion forces, which are present in a system containing kaolinite in the clay OH-Na form, plus the excess electrolyte, NaOH, greatly exceed and consequently overcome the effect of the attraction forces so that the system, as has been shown, should approximate more closely the viscous or true liquid than the plastic flow. It is possible, therefore, to improve the plasticity in the kaolinite–water system by adjusting the counterions in the diffuse double layer and the ions of the medium, which ultimately control the attraction forces in the system. This adjustment necessitates a new concept of the underlying causes of plasticity in suspensions of solid matter.

III. Fundamental Causes of Plasticity

In the preceding discussion, the writers have attempted to show that the plasticity of kaolinite slips, as exemplified by the yield point, depends on the attraction force present at the edge of the hypothetical lyosphere or water hull of the colloidal micelle. The causes of plasticity can now be discussed from the standpoint of these fundamental principles.

(1) The Electrical Double Layer

The most important single cause for the yield value of the kaolinite–water systems probably is the diffuse electric double layer associated with the solid particles or nuclei. The nature of this double layer and the reasons for its formation can furnish data which will be useful in a consideration of the plastic properties of other systems.

Kaolinite, according to its crystallographic classification, belongs to the monoclinic system and it displays good cleavage. In the formation of fragments, the fracture occurs along the basal cleavage plane and normal to it, forming thin hexagonal platy particles, but fracture along the cleavage plane does not cause the rupture of primary valence bonds. In a fracture parallel to the *c*-axis of the crystal unit, however, it becomes necessary to break the bonds between Si and O, Al and OH, or O.[5] These broken bonds serve as the basis for the preferential adsorption of hydroxyl ions.[3] The fact, moreover, should not be overlooked that these hydroxyl ions may be bonded by dipolar bonds to the oxygens of the basal silica sheet. In order to set up a negative charge on the particle, the location and mechanism of an attachment of anions on the surface of the particle is irrelevant. The hydroxyl ions that are thus adsorbed carry with them water molecules (hydration) which, as has been previously stated, make up part of the water hulls. This particle and the cations which swarm about constitute the Gouy-Freundlich diffuse double layer.

The crystallographic arrangement of the ions or atoms in certain substances, for example, the silver halides, causes the ions located on the surface, corners, and edges to be likewise unsaturated and gives rise to the preferential adsorption of oppositely charged ions on those materials.[1] A consideration of the plastic properties of any mineral should therefore include a careful analysis of the characteristics of the double layer formed by the particular substance under question. This analysis is highly important because, if the plasticity of a substance depends on the particular attraction forces between unsaturated valence bonds and the adsorbed ions, complete information about all of the ions in the system should furnish data relating to its plastic properties (as has been shown for kaolinite).

(2) Particle Size and Surface Area

The size of the particle exhibiting plasticity is of interest only insofar as it affects the attraction forces between the adsorbed ions and the unsaturated valence bonds of the particle. Inasmuch as the limit of size assigned to a colloidal particle is arbitrarily set at a value where such surface forces predominate (without being affected by any forces due to the mass of the particle), it is this size which governs the dimensions of the particles exhibiting plasticity. According to the preceding observations, for example, plastic flow and plasticity of suspensions are colloidal phenomena, and particles of colloidal dimensions, therefore, are obviously necessary in the system to permit this property or any colloidal property to manifest itself. Depending, then, on the nature of the material (a shape factor must be introduced), the size of the particle and its relation to the total surface area must be considered.

In the case of kaolinite, an average equivalent spherical diameter of less than 4 microns appears to be necessary before plastic properties are present.[6] Such an equivalent size is far above the arbitrary value set for the upper limit of the colloidal range. Kaolinite particles, however, exist in the form of plates, one dimension of which is well within the colloidal range. The surface along this particular dimension is sufficiently active to cause the colloidal phenomenon of plasticity to begin to manifest itself.

In the case of fibrillar particles, two dimensions may lie within the colloidal range but the third one does not. In the corpuscular system, all three dimensions of the particle must be within the colloidal range. The factor of size is therefore important, and careful consideration must be given to this variable in any study of colloidal characteristics.

The plastic properties of the clay mineral, attapulgite, have been found to be in full accord with its fibrous, crystalline structure.

(3) Effect of Concentration of the Solid Phase

"Plasticity" has been defined as the ability of a body to retain part or all of its deformation after the deforming stress is reduced to zero.

The term "workability" also includes this property. For any given clay–water system exhibiting elastico-plastic flow, an optimum yield value is obtained at a definite ratio of solids to water, which is an important factor in commercial processes. The phenomenon of elastico-plastic flow, however, is present in the clay–water system to a certain degree even at such low concentrations of clay that the system is unsuitable for ceramic use. Thus, a 1 to 2% suspension of clay in water and also a system containing 70 to 75% of clay exhibit elastico-plastic flow. From a ceramic viewpoint, however, the system which contains a 1 to 2% clay suspension in water is not considered to exhibit practical plasticity. The term "plasticity" as commonly used in ceramics, therefore, depends on the concentration of the solid phase of a system which exhibits elastico-plastic flow.

IV. Plasticity of Bentonites

The term "bentonite," as stated previously, refers to a rock formation composed largely of members of

[5] Linus Pauling, Nature of Chemical Bond and Structure of Molecules and Crystals. Cornell Univ. Press, Ithaca, N. Y., 1940. 429 pp.; *Ceram. Abs.*, 19 [1] 28 (1940); see also footnote 1.

[6] H. Whittaker, "Effect of Particle Size on Plasticity of Kaolinite," *Jour. Amer. Ceram. Soc.*, 22 [1] 16–23 (1939).

the montmorillonite group of clay minerals. Most of these minerals, furthermore, do not conform to the ideal structure, and lattice substitutions frequently occur. These substitutions result in establishing net residual negative charges in certain sections of the lattice which, in turn, cause cation attraction. Sodium is the most common cation found in naturally occurring American bentonites. The crystal units of montmorillonite are only loosely held together by weak O–O bonds. The sodium ions are primarily adsorbed on the surfaces of the silica sheets and to a negligible extent only on the fractures along the *c*-axis. When hydration occurs, these ions pry the particles apart and form double layers of appreciable thickness. The clay exhibits a high degree of swelling. This assumption has been substantiated by X-ray diffraction patterns, revealing a so-called "expanding lattice" along the *c*-axis of the mineral.[1] Because the structure and the properties resulting therefrom are far more complex in montmorillonites than in kaolinite, it is difficult to undertake a complete discussion of the plastic properties of bentonite, but some aspects of it may be pointed out.

In the formation of bentonite particles, fractures parallel to the *c*-axis, similar to those occurring in the kaolinite crystal, seldom take place. On these surfaces, a diffuse double layer, identical with that obtained with kaolinite, can theoretically be formed, that is, first a layer of preferentially adsorbed hydroxyl ions and then the counterions in a diffuse arrangement. The presence of hydrogen as the counterion, for this condition, would give the greatest attraction force at the edge of the water hull and therefore the greatest plasticity, all other factors being constant. The least plasticity should be exhibited when sodium ions serve as countercharges for the preferentially adsorbed hydroxyl groups for the same reason as that given for kaolinite.

Even if such a theoretical adsorption at the broken edges should occur, however, its effect would be negligible in comparison to that caused by the cations, which are adsorbed on the cleavage planes, because of the negative charge of the lattice.

Although no detailed systematic studies of the plasticity of bentonites have been reported, it is reasonable to assume that their results will be similar, at least in principle, with those discussed for kaolinite. It must naturally be remembered that the particle structure, location, and cause of net charges on the particle surface and, consequently, the distribution of counterions are not the same and that the average size of the bentonite particles is smaller than those of kaolinite. There seems to be sufficient evidence, however, to assume that an H bentonite will be the most plastic and an Na bentonite the least plastic.

V. Conclusions

Because most industrial clays which contain kaolinite as the principal mineralogic constituent contain calcium in exchange positions, these clays are relatively plastic. They may be used, therefore, in most commercial processes after the addition of the proper amount of tempering water and suitable mixing. The particle-size distribution of such crude clays must contain sufficient amounts of material of an equivalent spherical diameter or less to bring about the attraction forces necessary for plasticity. If it were necessary, for some reason, to enhance the yield point of a kaolinitic clay, the exchange of the calcium counterions for aluminum or hydrogen ions would be the most economical method. Because the introduction of the monovalent hydrogen ion or of trivalent ions causes a further reduction of the charge on the particles, the attraction forces acting between the micellae are increased, thereby increasing the plasticity of the system.

A systematic study of the plastic properties of other clay minerals and of the so-called nonplastic materials, in relation to the present discussion, is essential and would reveal interesting results. If plasticity is a colloidal phenomenon (as the writers have attempted to show), it is entirely possible that, after the proper adjustments of certain variables have been made in systems which heretofore have not displayed plasticity,[7] this property will reveal itself. It should also be possible, however, to change a plastic system to a nonplastic system by appropriate adjustment of certain variables, which means that any degree of deflocculation (dispersion) of the system may be achieved.

Additional References

R. Houwink, Elasticity, Plasticity, and Structure of Matter. University Press, Cambridge, England, 1937. 374 pp.; *Ceram. Abs.*, **17** [6] 235 (1938).

G. A. Bole, "Mechanism of Plasticity from a Colloid Standpoint," *Jour. Amer. Ceram. Soc.*, **5** [8] 469–77 (1922).

Acknowledgment

The authors are indebted to F. H. Norton for helpful suggestions relating to the rheological terminology and definitions.

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[7] E. O. Wilson, "Plasticity of Finely Ground Minerals with Water," *Jour. Amer. Ceram. Soc.*, **19** [4] 115–20 (1936).

CONDITIONS ENCOUNTERED IN FILLING PRESSURE WARE*

By John M. Sharp

Abstract

Many beverages contain dissolved CO_2 which is held in solution by pressure above atmospheric. To fill these products into pressure ware calls for mechanical systems which operate at pressures above atmospheric. The bottles are thus subjected to varying conditions of internal pressure during their filling. Because the ware is usually warmer than the product, there may also be some thermal effect. The action of the filling machine and the closure application may introduce some mechanical loading. The extent and timing of these conditions depend somewhat on the type of the filling apparatus, but the general limits may be stated to give some estimation of the service demands on the ware during this particular operation.

I. Introduction

A large proportion of the bottles classified as pressure ware goes into service as containers for beverages. Many of the beverages contain dissolved carbon dioxide, which is attendant with moderate pressure above atmospheric. The handling conditions which this type of ware may encounter outside the bottling plant vary with various localities and have been partially reported by other workers. The conditions encountered in the bottling plant may be classified into those which are subject (1) to operator control (that is, mechanical effects of conveying and handling or the thermal, chemical, and mechanical phases of bottle washing) and (2) to inherent machine design, such as the filling and closure application (crowning) cycles. The conditions subject to control by the operator have been partially reported, but little work has been published on the internal-pressure, thermal, and mechanical effects occurring in the filling and crowning cycles which are considered in this paper.

II. Internal Pressure

Those beverages having dissolved carbon dioxide in appreciable quantities will exert pressures above atmospheric in the bottles containing them. Table I gives the saturation pressures of carbon dioxide in water for typical gas contents. The amounts of carbon dioxide dissolved are generally spoken of as volumes (that is, volumes of carbon dioxide gas at standard temperature and pressure per volume of water), which is the same solubility factor as Bunsen's alpha. A beverage of low carbonation may fall in the range of about 2.5 volumes; those of medium carbonation, 3.5, and those of high carbonation, 4.5. Slight variations from these pressures may occur in products which are composed of substances in addition to water, although these variations, in general, do not materially influence the trend. These amounts of carbon dioxide are in the supersaturation range when considered at atmospheric pressure and therefore must have pressure above atmospheric maintained during handling and filling for their retention. In accordance with the general gas-absorption laws, the pressure needed increases with rising temperature; this is definitely shown in Table I. The temperature therefore materially influences the amount of handling pressure needed; the actual operation pressure may be higher than this minimum because of (1) mechanical agitation or turbulence, (2) the presence of foreign gases, and (3) the varying efficiency of the gas-absorbing units (carbonators).

Table I

Saturation Pressures of Carbon Dioxide in Water

(°F.)	Vol. of carbon dioxide/vol. of water* 2.5	3.5	4.5
	Pressure (lb./sq. in.) gauge		
40	11	21	31
60	22	37	52
80	36	56	77
100	51	78	104

* Bunsen's α.

In this respect, it is interesting to note that the lower range of carbonation, about 2 volumes, gives a minimum pungency, whereas the higher limit, approaching 4.5 volumes, in general is the maximum load of supersaturation which the typical product can carry under normal handling and dispensing. Products of high carbonation can produce, with increased temperature, the maximum pressures which the crown closure can be expected to retain because such closures will normally tend to vent on a gas seal at pressures of 100 to 160 lb. per sq. in., depending on the quality of the sealing disk and on its seating on the locking ring of the bottle.

The important factors relating to the gas content in this discussion are (1) at higher temperatures, higher pressures are needed to retain a given gas content (carbonation) and (2) rough or rapid handling (turbulence) definitely promotes the instability of the contained carbon dioxide in the beverage. These factors definitely influence the operation of filling machines.

III. Thermal Effect

Practically all bottles, whether one trip or refillable, are first given a cleaning and commercial sterilization in warm (130° to 160°F.) alkaline detergent solutions, followed by a rinse with potable water. The rinse may be the temperature of the water service line, cooling the

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Glass Division). Received July 1, 1941.

bottles to temperatures of 60° to 80°F., as received at the filler (often warmer under irregular control). The thermal effect during filling depends on the difference in temperature between the bottle and the liquid being filled into it, the rate at which the liquid is delivered, and the directness of contact of the liquid with the more thermally sensitive areas, such as the base. Inasmuch as the bottles are usually warmer than the liquid, there is a tendency for tension to develop on the inside surface. Most fillers tend to deliver the liquid down the wall of the bottle from a delivery tube inserted through the neck. The directness of contact of the liquid with the base may be reduced if a portion of syrup (throw) has first been dispensed into the bottle. These factors, of course, depend somewhat on the exact filler design as well as on the product being filled. If the bottles are pasteurized after they are filled, there will be additional thermal effect although it usually occurs at a lower differential.

IV. Mechanical Effect

The mechanical effect is primarily a vertical loading if the impact or other loads in the conveyer and feed mechanism are not considered. The filler head, which dispenses the liquid into the bottle, usually exerts only slight loading, but this may be disregarded unless the bottle is of irregular proportions. The crowning operation brings about a major loading as the crown closure is applied and seated after the contents are delivered into the bottle. The crown, with its fluted skirt opened, is placed over the locking ring of the bottle finish. The actual locking of the skirt results from a tapered sleeve descending over the periphery of the crown and deforming the flutings to fit the external contour of the finish. Varying with the mechanical design of the crowner, there may be, in addition, a central plunger or stamp which first places a vertical pressure on the crown so that the sealing disk is brought into elastic compression and holds it in this position until the fluted skirt is locked by the descending concentric sleeve. The maximum vertical loading which may develop on the bottle is controlled by a heavy coil spring backing up the crowner throat (in some instances the table under the bottle may have a spring or plunger for the same purpose). This loading, in practice, is about 400 lb. or less, although occasionally a maximum of about 750 lb. occurs. Any irregular placement of a bottle or any irregularities in the bottle, however, may give excessively high localized values.

V. Bottle Filler Classification

Some popular terminology has attempted to classify all machines as "high" or "low" pressure fillers, but it has proved to be relatively inaccurate, particularly relating to the process of filling the bottles. Careful observation of most of the machines in common use shows that they may be placed in two general classifications with some subheading employing a distinction based on their cycle of action.

The first group may be called "coincidental" fill-crown, inasmuch as the bottle receives its portion of carbonated water (or beverage) and its crown at the same location in the machine, all within a few seconds. During the cycle, the bottle is sealed by a rubber cushion seated on the reinforcing ring, a counterpressure is built up in the bottle, and the carbonated water is delivered by a metered pump against this counterpressure through a delivery tube inserted into the bottle. The delivery tube then rises, and the crown slides over the locking ring of the bottle finish, in which position it is crimped by a descending crowning sleeve, while the counterpressure is being continuously maintained. These units usually have only one filling head, and they are employed for moderate output.

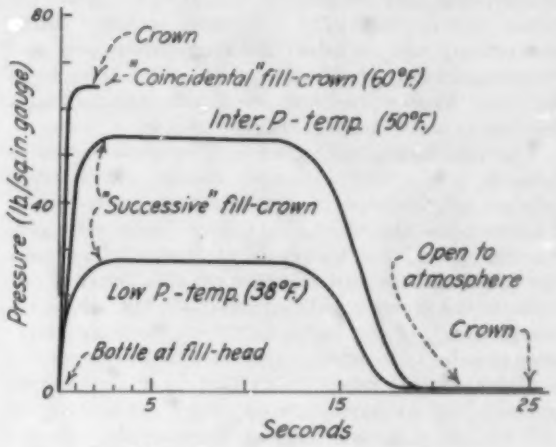

FIG. 1.—Typical filling-crowning cycles of bottle-filling machines; beverages approximately $3^1/_2$ volumes of CO_2 and bottles of 6 to 8 fluid-ounce capacity.

The second group may be called "successive" fill-crown, inasmuch as the bottle progresses through the counterpressure, filling, release of pressure, and final crowning in progressively changing positions, usually taking more than 20 seconds for the series of operations. In the cycle, the counterpressure on the bottle is released before the crown closure is applied to the finish; definite stability of the liquid is required to prevent "boiling over" before crowning, accomplished by using cooled water or beverage with the resulting lower gas pressure. One type of machine in this classification has a valve system that allows relatively low-pressure liquid handling and delivery, but it requires stable carbonation, which is usually obtained by maintaining liquid temperatures at about 40°F. A machine of this type may be designated as low pressure-temperature (low P.-temp.) under this major classification. The other type, with a different valve system, may operate at slightly higher liquid temperature (usually 45° to 55° F.) with a correspondingly higher pressure, and this type may be designated as intermediate pressure-temperature (inter. P.-temp.) under the major classification. These machines are usually of the rotary table, multiple-head type; they have reasonably high output, and most of them have separate crowning heads which operate at moderate speed.

VI. Typical Examples

The existing differences between these types of machines are shown by the data given in Fig. 1, which are based on comparable observed plant operation. Similar products in each case are being filled into "split" sized bottles (6 to 8 fluid-ounce capacity) with 3.5 volume carbonation. The coincidental fill-crown unit, operated with water at 60°F., showed a filling pressure of 65 lb. per sq. in. (p.s.i. gauge) and delivered the water into the bottle in approximately $1^1/_2$ seconds; the crown was applied while the pressure was still maintained with a rapid crowning thrust. With the successive types, the water-delivery time was approximately 15 seconds in each case, and the pressure was released before the crown was applied. The differences occurred in the temperature and pressure; the intermediate pressure-temperature unit used water at 50° and a pressure of 55 p.s.i., whereas the low pressure-temperature unit used water at 38° and a pressure of 28 p.s.i.

The coincidental fill-crown unit in these instances tends to give a higher internal pressure with a given product, and the rate of pressure build-up is very rapid. Inasmuch as this unit can operate with relatively warmer water, the temperature differential between the bottle and the cool water may not be extreme, but because the water is delivered rapidly, the actual accommodation of the bottle to the temperature difference may be very sudden; this effect will be increased if colder water is used. Note that while the internal pressure is at its maximum and while there is probably still existing a definite thermal difference the crown is applied with a quick thrust so that the effects of pressure, thermal shock, and mechanical loading occur within a relatively short space of time.

In distinction, the successive fill-crown units take slightly longer to build up their counterpressure, the maximum pressures are not so high, and the accommodation to the temperature difference by the bottle will probably be more gradual because the water is delivered over a longer period of time. The bottle probably has recovered from most of the thermal effect, and the counterpressure has been released from the bottle before the crown is applied so that, in this instance, these three effects follow in gradual succession. In the two subclassifications, the distinction is based on the differences in water temperature and on the attendant necessary counterpressures.

The effects which occur during the filling-crowning steps are determined by these genera' conditions. Larger bottles require longer liquid delivery periods. Products of higher or lower carbon dioxide content will show corresponding differences in internal pressure on the ware during the filling. The thermal effect will be present, irrespective of pressure, causing tension on the inside of the ware when the product is colder or on the outside when the product is hotter than the ware. The mechanical loading depends greatly on the crowner. As is characteristic of many of these types of machines, their behavior and satisfactory operation is always expedited by good mechanical maintenance and repair.

VII. Conclusion

The various conditions of internal pressure, thermal shock, and mechanical loading which may occur when pressure ware is filled with beverages has been described. The extent of these factors and their timing depends on the type of beverage being filled and on the type of filling machine being used. These conditions are basically inherent to the product and the machine, although good mechanical adjustment aids materially in the operation.

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LOW-TEMPERATURE VITREOUS BODIES*

By C. J. Koenig

Abstract

The properties of a series of low-temperature bodies predominately comprised of clays and nepheline syenite are described. These bodies have a higher alumina content than the usual typical pottery bodies because of the high alumina content of nepheline syenite and clays and also because flint is introduced only in small amounts.

I. Introduction

This investigation relates to the development of low-temperature vitreous bodies for single-fire whiteware products. The production of flatware from these low-temperature bodies first necessitates the development of glazes which have abrasion- and corrosion-resistance properties equal to that of present dinnerware glazes but which mature at about five cones lower than the body matures.† Providing the quality and simplicity of production of a given product is not

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (White Wares Division). Received October 28, 1941.

† An investigation on the development of abrasion- and corrosion-resistant glazes maturing at low temperatures is now in progress at the Engineering Experiment Station.

Dinnerware is being produced on a commercial basis from this type of body, but data relating to the glazes being used are not available.

sacrificed, it is advantageous to fire the ware at a lower temperature. Among such factors are (*a*) reduced firing time, (*b*) lower fuel cost, and (*c*) a wider color range of glazes and bodies. Many small art potteries and art studios, moreover, do not have the proper equipment to fire ware to a temperature high enough to produce a white vitreous product. Previous tests have shown that nepheline syenite starts to sinter at a low temperature (see Fig. 1) and is vitreous about four cones

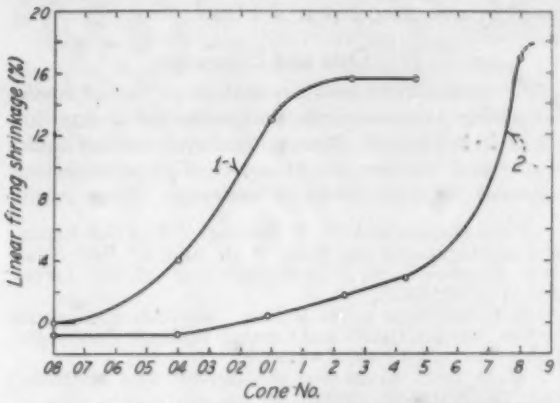

FIG. 1.—Firing shrinkage: curve 1, Lakefield nepheline syenite curve 2, North Carolina potash feldspar.

below its P. C. E.[1]; this property of vitrification at a relatively low temperature has been used to advantage. Another property peculiar to nepheline syenite is its small variation in thermal expansion which it exhibits with the difference in thermal history.[2] The thermal expansion of crystalline nepheline syenite is higher than that of clays or of crystalline potash feldspar so that even though nepheline syenite is only partially fused at cone 2, it contributes more to raising the expansion of the body than do the clays or the feldspar. The use of flint raises the thermal expansion of a body, but this property is partly offset by the relatively high crystalline expansion of nepheline syenite. Flint was not incorporated or it was introduced only in small amounts in these test bodies for the following reasons: (1) In order to add a sufficient amount of clay, it was necessary to have the nonplastic portion comprised essentially of nepheline syenite if vitrification was to be reached around cone 3 without recourse to an auxiliary flux; and (2) the warpage resistance depends largely on maintaining a high viscosity in the glassy phase in bodies with a high flux content, and it was hoped to attain this condition by having a high alumina content, inasmuch as nepheline syenite in itself has a relatively high amount of alumina. Additions of alumina to nepheline syenite raise the P. C. E. of such mixtures rapidly, and as the glassy phase in this type of body is essentially fused or partially fused nepheline syenite, the solution of even a small amount of additional alumina obviously would exert a strong influence on the maintenance of a high viscosity during firing, which in turn would provide a good maturing range.

Figures 2 and 3 are taken from the unpublished work of McRitchie,[3] who states that because nepheline syenite is unsaturated with respect to silica it is natural to find that the lines sweep down toward the flint corner of the field. Additions of kaolin to nepheline syenite, however, cause a rapid increase in the P. C. E. of such mixtures.

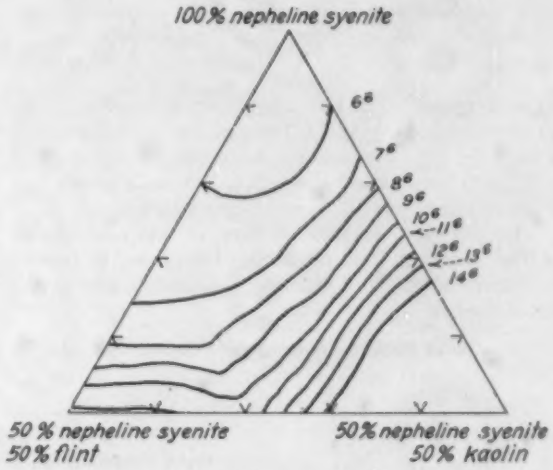

FIG. 2.—Cone deformation of mixtures of nepheline syenite, flint, and kaolin.

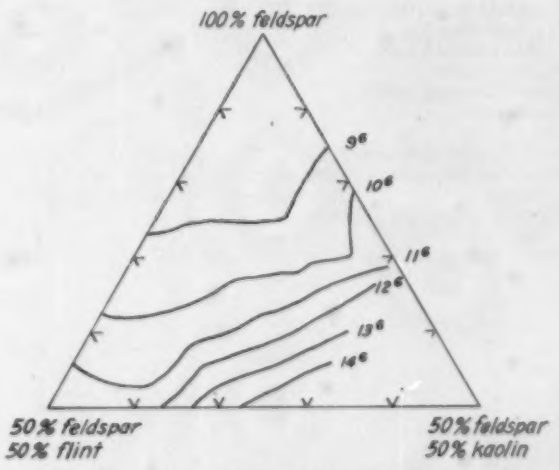

FIG. 3.—Cone deformation of mixtures of feldspar, flint, and kaolin.

II. Experimental Procedure

The chemical composition and screen analyses of Lakefield nepheline syenite are given in Table I.

Seven thousand grams, dry weight, of the bodies

[1] C. J. Koenig, "Fundamental Properties of Nepheline Syenite," *Jour. Amer. Ceram. Soc.*, **22** [2] 35–38 (1939).

[2] H. J. Orlowski and C. J. Koenig, "Thermal Expansion of Silicate Fluxes in the Crystalline and Glassy States," *ibid.*, **24** [3] 80–84 (1941).

[3] Frank H. McRitchie, "Cone Deformation Study of High Flux Area in the Nepheline Syenite–Flint–Kaolin System." Thesis submitted to the faculty of the University of Saskatchewan, 1940.

TABLE I

NEPHELINE SYENITE CHEMICAL COMPOSITION AND SCREEN ANALYSES

	(%)		(%)
SiO_2	60.24	MgO	0.02
Al_2O_3	24.05	Na_2O	10.03
Fe_2O_3	0.06	K_2O	5.01
TiO_2	0.002	Ignition loss	0.46
CaO	0.15	Total	100.022

Screen analyses

Mesh size	Residue (cumulative %)
140	0.10
200	0.90
270	3.00
325	5.20

were prepared. The ball clays were crushed to $^1/_2$-in. size and soaked overnight, blunged for about 3 hours in a propeller type of blunger at a specific gravity of about 1.30, and then passed through a 100-mesh screen and dried in plaster molds to wedging consistency.

The standard methods, apparatus, and calculations of The American Ceramic Society[4] were used in general to determine water of plasticity, shrinkage, and modulus of rupture.

[4] Standards Report, *Jour. Amer. Ceram. Soc.*, 11 [6] (1928).

The percentage linear thermal-expansion determinations were made on fired bars with a fused-quartz expansion apparatus designed by the National Bureau of Standards.[5]

Glaze-compression data were obtained by the ring-test method, which was originated by Schurecht and Pole[6] and amplified by Bell.[7]

Firings were conducted in commercial kilns except for that at cones 1 to 2. In the laboratory firing, the end point was approached at about 50°F. per hour followed by a soaking period of 1 hour.

III. Data and Discussion

The compositions and physical properties of bodies containing clays and nepheline syenite but no free flint are given in Table II. Because the clay content of bodies Nos. 1 to 4 was low, the plasticity of these mixes was bolstered by the addition of bentonite. These bodies

[5] Peter Hidnert and W. T. Sweeney, "Thermal Expansion of Magnesium and Some of Its Alloys," *Bur. Stand. Jour. Research*, 1 [5] 771–92 (1928); R. P. 29; *Ceram. Abs.*, 8 [1] 65 (1929).

[6] H. G. Schurecht and G. R. Pole, "Methods of Measuring Strains Between Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, 13 [6] 369–75 (1930).

[7] W. C. Bell, "Evaluation of Glaze-Fit Test Methods," *ibid.*, 23 [6] 163–66 (1940).

TABLE II

BODY COMPOSITION AND PHYSICAL PROPERTIES

Body composition	Body No. 1	2	3	4	5
Lakefield nepheline syenite	88.5	80.0	70.0	65.5	52.0
Ky. ball clay No. 4	10.0	19.0	20.0	8.0	16.8
Edgar plastic kaolin			10.0	5.0	8.3
Kamec kaolin				13.0	
Harris Lunday kaolin				8.0	
Bentonite	1.5	1.0		0.5	
Ga. kaolin					10.4
VCI English china clay					12.5
Water of plasticity (% dry basis)	23.2	21.3	22.3	25.0	29.8
Drying shrinkage (% dry basis)	4.4	3.8	3.7	4.7	6.5
Dry strength (lb./sq. in.)	540	470	420	360	500
Cone No.	Linear firing shrinkage (% dry basis)				
06	2.1	2.2	2.8		
01–02				4.8	7.3
01	5.8	5.4	5.8		
1				7.5	
1–2	9.7	9.4	9.6		
3					8.9
3–4	9.7	9.4	9.6		
	Absorption (%)				
06	13.5	11.9	12.3		
01–02				10.1	4.7
01	6.8	5.9	6.8		
1				4.0	
1–2	1.1	1.2	1.1		
3				1.0	0.3
3–4	0	0	0		
	Modulus of rupture (lb./sq. in.)				
06	3,660	3,750	3,700		
01–02				4,500	7,100
01	6,000	5,750	6,600		
1–2	11,100	11,200	11,300		
3				7,200	9,000
3–4	9,400	9,900	9,700		

had satisfactory dry-strength values, ranging from 360 lb. per sq. in. for body No. 4 to 540 lb. per sq. in. for body No. 1. Body No. 5, which contained the most clay and no bentonite, had a dry strength of 500 lb. per sq. in.

It is interesting to note that body No. 1 (11.5% of clay) and body No. 3 (30% of clay) had the same percentage of absorption when they were fired to cones 1 to 2. Nepheline syenite alone is vitreous at these cones, and it can carry 30% of tight-firing clays and still vitrify at this temperature.

Body No. 3, fired to cones 1 to 2, had a cross-breaking strength of 11,300 lb. per sq. in., but at a higher fire (cones 3 to 4), the strength dropped to 9700 lb. per sq. in.

Figure 4 shows the thermal expansion of bodies Nos. 1 to 3, fired at cones 3 to 4. Increasing additions of clay lowered the thermal expansion as was to be expected. Figure 5 illustrates the variation in thermal expansion of body No. 3 (70% of nepheline syenite and 30% of clay) with the indicated differences in thermal history. The thermal expansion increased with increased firing temperature. This is a cumulative trend and is the result of the properties of nepheline syenite and of the clays although the clays have the greater effect on this property.

All of the bodies comprised of nepheline syenite and clays approached vitrification at about cone 2 regardless of whether 11.5% or 30% of relatively tight-firing clays were present. In the next series of bodies, an effort was made to determine the quantity and type of clays which could be added to nepheline syenite to produce a good casting body and yet not increase the maturing point appreciably above the temperature at which nepheline syenite vitrifies alone. Body No. 4, which had a clay content somewhat similar to a commercial hotel chinaware body, typifies this series. At cones 1 to 2, its absorption was 4% as compared to 1.2% for the bodies of the first series. Body No. 5

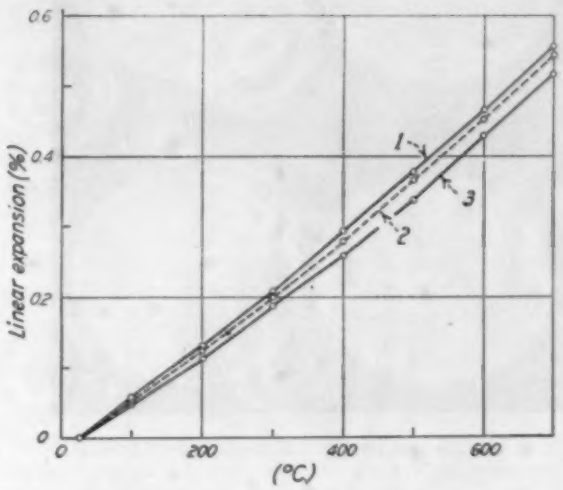

FIG. 4.—Thermal expansion at cones 3 to 4 for body specimens, curves 1, 2, and 3.

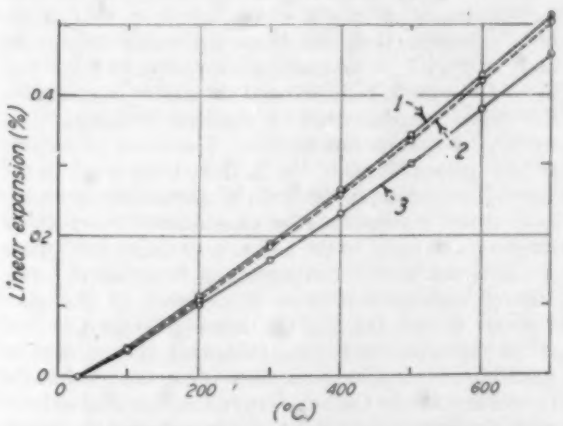

FIG. 5.—Influence of firing temperature on thermal expansion of body No. 3 (nepheline syenite 70% and clay 30%); curve 1, cones 3 to 4; curve 2, cone 1; curve 3, cone 06.

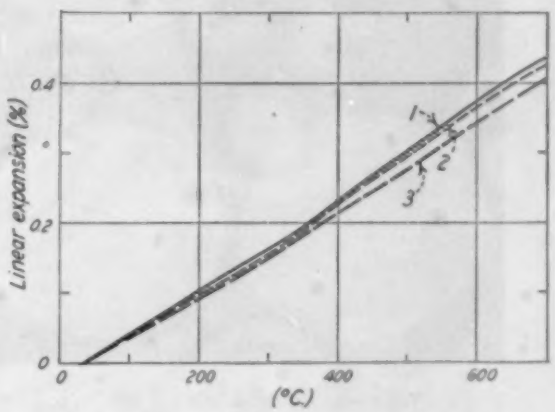

FIG. 6.—Influence of firing temperature on thermal expansion of body No. 5; curve 1, cone 3; curve 2, cones 1 to 2; and curve 3, cones 01 to 02.

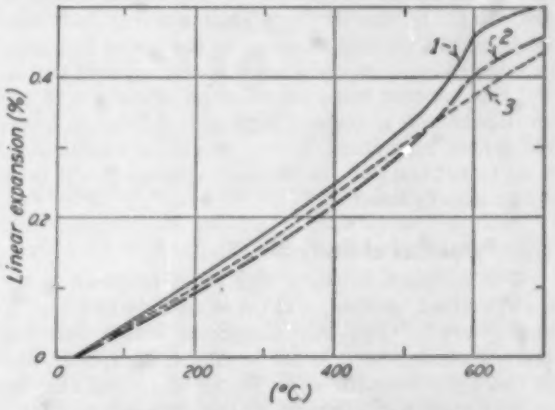

FIG. 7.—Comparison of thermal expansion of low-temperature vitreous body No. 5 with that of typical hotel chinaware and semivitreous dinnerware bodies; curve 1, semivitreous body; curve 2, hotel china body; curve 3, cone 3, vitreous body No. 5.

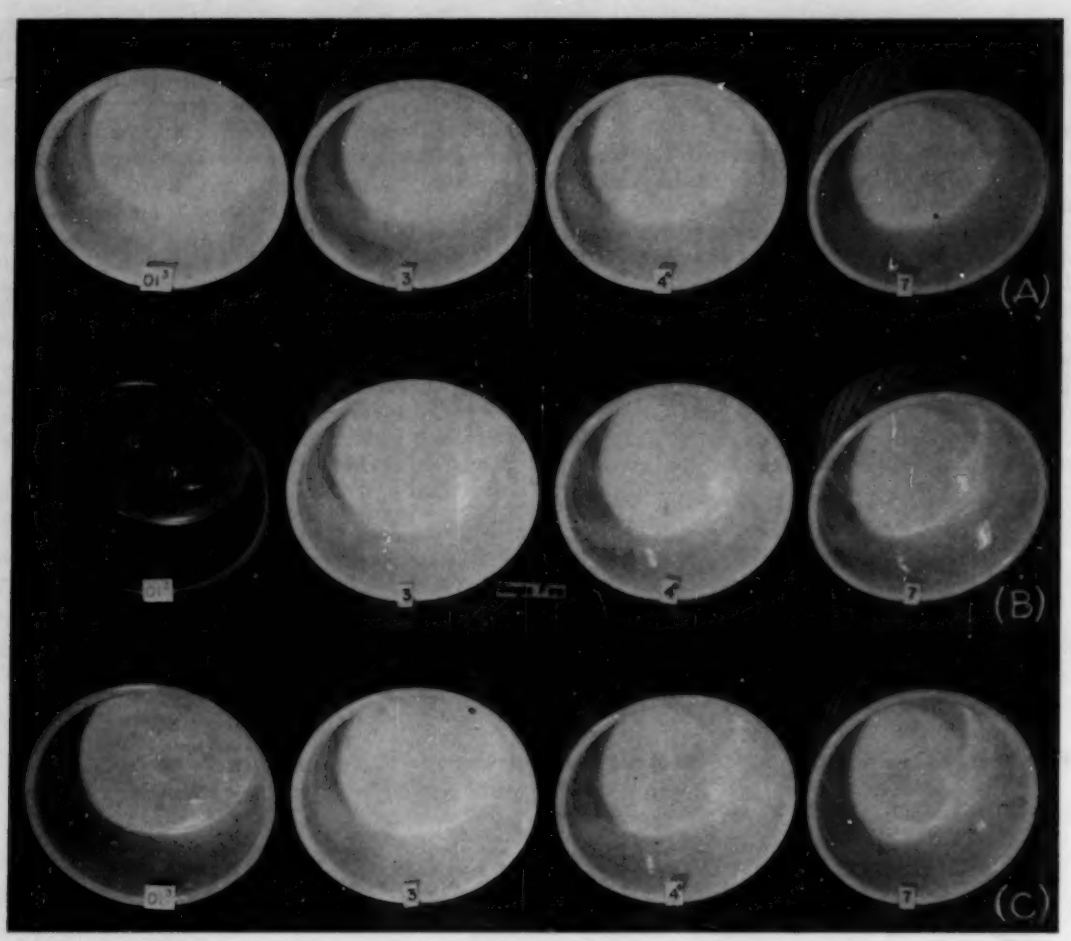

FIG. 8.—Ware made from body No. 5, fired to cones 01^3, 3, 4^4, and 7, respectively; (*A*) bisqueware, (*B*) single-fireware, and (*C*) two-fireware.

had a higher clay content than No. 4 although it vitrified at an earlier temperature owing to the nature of the clays. In this series, a good working body was being sought without recourse to the use of bentonite or other plasticizers, although it was recognized that as the clay content was increased the advantage of the small variation in thermal expansion in relation to the differences in thermal history would be sacrificed to some extent and that the thermal expansion of the body would also be lowered.

(1) Properties of Body No. 5

A 65-lb. batch of body No. 5 was prepared in the usual manner, deaired, and taken to a pottery for jiggering bowls. The head jiggerman stated that this body worked as well as the regular commercial body. It had a dry strength of 500 lb. per sq. in. and a drying shrinkage of 6.5% (which is about the average for a semivitreous dinnerware body), its absorption at cones 01 to 02 was 4.7%, and it was vitreous at cone 3. Its fired strength at cones 01 to 2 was 7100 lb. per sq. in. and at cone 3 it was 9000 lb. per sq. in.

The thermal expansion of body No. 5, fired to three different temperatures, is given in Fig. 6, and its thermal expansion at cone 3 is comparable to that of the hotel chinaware body and the semivitreous dinnerware body in Fig. 7. The thermal expansion of body No. 5, fired to cone 3, falls between the curves representing the typical expansivities of commercial hotel chinaware and semivitreous bodies. Inasmuch as no free silica is present in body No. 5, there is no break in the thermal-expansion curve at 573 °C. because of the alpha-beta quartz inversion. The expansion is lower above the inversion point in the bodies containing free quartz owing to the negative expansion of beta-quartz. This reduced expansion is more pronounced in the semivitreous bodies than in the hotel chinaware bodies. If the glazes are rigid above this point, they tend to be placed in a state of tension which is counteracted at the inversion point by the large expansion that is associated with the inversion. Below its transformation point, a glaze which has a lower thermal expansion than body No. 5 (whose expansion curve is straight) would be placed under progressively increasing compression

TABLE III
CRAZING RESISTANCE OF COMMERCIAL GLAZES ON BODY NO. 5

Process	Cone No. 01–02	3	4[a]	7
Single-fire	Crazed after standing several days	50% failed in autoclave	Failed in autoclave	Passed autoclave
Two-fire	Same as above	Passed autoclave	Passed autoclave	Passed autoclave

as the ware is cooled. It would seem that a body of this type could be safely cooled at a faster rate than a body possessing a relatively abrupt change in expansion at 573°C.

Samples of ware made from body No. 5 and fired to four different temperatures are shown in Fig. 8. This body was free from warpage at cones 01 to 02, but it had an increased tendency to distortion as the temperature was raised.

Figure 8 (*B*) shows ware that was glazed and single fired, using the commercial glazes of the plants at which the samples were fired; Fig. 8(*C*) shows ware that was first bisque fired and then glost fired at the same cone. The autoclave schedule was $^1/_2$ hour up to 150 lb. of pressure, 1 hour at 150 lb., and $^1/_2$ hour to release the pressure. Table III shows the crazing resistance of commercial glazes used on body No. 5.

When body No. 5 is fired to cones 1 to 2, it should make a good body for pottery and certain other types of ware; its absorption of 1 to 2% at this cone is sufficiently low so that there would be little or no danger of moisture expansion. In a body containing a high flux content, the resistance to warpage is governed largely by the viscosity of the glassy phase. This type of body is unusual in that vitrification is attained about four cones below the P. C. E. of nepheline syenite. In a Parian type of body, which usually contains 60 to 70% of feldspar and with clay as the other ingredient, the firing was conducted near or above the P. C. E. of the feldspar.

(2) Bodies Containing Small Amounts of Flint

A suitable single-fire product was sought, which could be fired to cones 3 to 4 and could be glazed with a regular semivitreous dinnerware glaze. Bodies Nos. 6, 7, and 8 were prepared for this purpose. In body No. 6, the thermal expansion was raised by increasing the nepheline syenite content, whereas this was accomplished in bodies Nos. 7 and 8 by introducing 4% and 10% of flint, respectively, to the bodies. The test specimens were formed by the casting process. Table IV shows the composition and physical properties of these bodies.

The thermal-expansion curves of bodies Nos. 6, 7, and 8 fired to cones 3 to 4 are shown in Fig. 9. Body No. 8, which contained 10% of flint, had the highest expansion, and the regular glaze applied on this body was under the greatest compression, namely, 0.10 mm., which is a satisfactory stress condition. Increasing the nepheline syenite content from 52 to 60% raised the expansion of this type of body more than the addition of 4% of flint. This increase was reflected in the glaze-compression values.

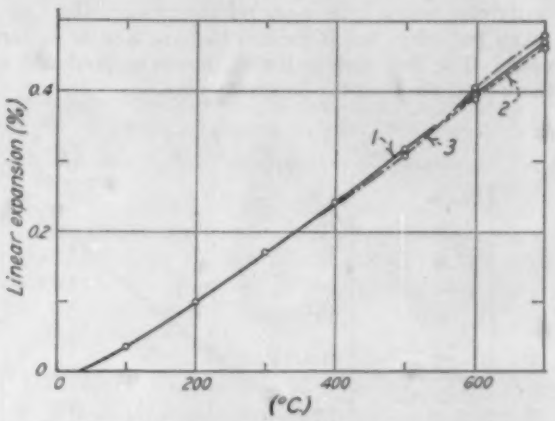

FIG. 9.—Thermal-expansion curves of body specimens; curve 1, body No. 6; curve 2, body No. 7; curve 3, body No. 8.

TABLE IV
BODY COMPOSITIONS AND PHYSICAL PROPERTIES

	Body No. 6	7	8
Lakefield nepheline syenite	60.0	52.0	50.0
Flint		4.0	10.0
Ky. ball clay No. 4	14.0	15.4	14.0
Pioneer Ga. kaolin	8.7	9.5	8.7
Edgar plastic kaolin	6.9	7.6	6.9
English china clay No. 30	10.4	11.5	10.4
Total linear shrinkage wet basis (%)*	12.6	12.6	12.2
Absorption (%)*	0	0	0
Ink stain*	None	Very slight	Very slight
Modulus of rupture (lb./sq. in.)*	8500	8200	8000
Glaze fit compression (mm.)*†	0.076	0.06	0.10

* Fired to cones 3 to 4.
† Commercial semivitreous dinnerware glaze.

(3) Bodies Using Only American Clays

The compositions, casting condition, and physical properties of bodies using only American clays are given in Table V, and Fig. 10 shows the thermal-expansion curves for bodies Nos. 12 and 13. It was necessary to fire about one cone higher to obtain vitrification when American kaolin was substituted for English china clay. Thus body No. 10 was vitreous at cone 4, whereas the bodies previously described showed a corresponding degree of vitrification when they were fired to cone 3. The fired colors of these bodies were satisfactory. Body slip No. 9, however, was too thixotropic for good casting conditions.

In bodies Nos. 10 to 13, the Harris Lunday clay was increased 2% at the expense of Edgar Plastic kaolin and Pioneer Georgia kaolin, and the nepheline syenite content was increased 2% at the expense of the ball clay. These latter four bodies were found to be satisfactory for drain casting.

Bodies Nos. 10 and 11 are the same except that No. 10 contains 16% of Kentucky Old Mine No. 4 ball clay and No. 11 contains 16% of Bell dark ball clay. The latter clay was a little more refractory than the Kentucky ball clay, but it seemed to have a little better color. The Bell dark ball clay, however, produced a more fluid slip than the Kentucky clay.

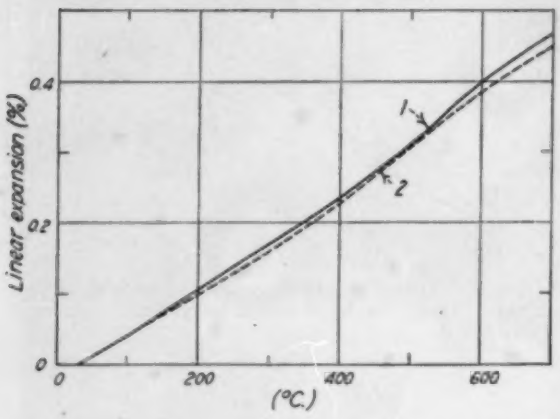

FIG. 10.—Thermal expansion at cones 3 to 4; curve 2, body No. 12 (pyrophyllite 6%) compared to curve 1, body No. 13 (flint 6%).

Bodies Nos. 12 and 13 were alike in composition except that No. 12 contained 6% of pyrophyllite and No. 13 had 6% of flint. The use of pyrophyllite was suggested to whiten the body. The fired colors of these bodies were in the same range, but body No. 12 (with pyrophyllite) seemed to have a slightly better color than No. 13. Little difference was noted between the fired absorption, strength, and shrinkage of these bodies. Body No. 12 had a little lower thermal expansion than No. 13 (see Fig. 10).

These bodies have an ivory tint which can be neutralized by the addition of cobalt stain. The addition of 0.015% of a commercial blue body stain to No. 13 resulted in a color which compared satisfactorily with some of the commercial hotel chinaware.

IV. Conclusions

Vitreous bodies which matured at cone 3 may be formulated from clays and nepheline syenite without recourse to an auxiliary flux. These bodies have a good firing range and ample strength.

TABLE V

BODY COMPOSITION AND CASTING AND PHYSICAL PROPERTIES

Body composition (%)	Body No. 9	10	11	12	13
Nepheline syenite	52	54	54	54	54
Flint	6	6	6		6
Pyrophyllite (Vanderbilt)				6	
Edgar plastic kaolin	9	8	8	8	8
Pioneer Ga. kaolin	9	8	8	8	8
Harris Lunday kaolin	6	8	8	8	8
Bell dark ball clay			16	8	8
Ky. Old Mine ball clay No. 4	18	16		8	8
Casting conditions					
Specific gravity	1.78	1.77	1.77	1.76	1.76
Electrolyte dry basis (%) (60% *N* sodium silicate and 40% Na_2CO_3)	0.12	0.11	0.12	0.10	0.10
Physical properties					
Linear drying shrinkage (% dry basis)	3.9	3.9	3.9	3.85	3.9
Firing shrinkage (% dry basis)					
Cone 2	8.46	8.6	8.5	8.5	8.5
Cone 3–4				8.7	8.7
Cone 4	8.7	9.1	9.0		
Absorption					
Cone 2	3.4	3.3	3.8	3.6	3.6
Cone 3–4				1.3	1.4
Cone 4	0.15	0	0		
Modulus of rupture (lb./sq. in.)					
Cone 2	6100	6400	6300	6500	6400
Cone 3–4				7900	7800
Cone 4	8000	8800	8700		

The higher the nepheline syenite content of the bodies the higher the thermal expansion and the smaller the variation in thermal expansion with difference in thermal history.

The addition of 5 to 10% of flint raises the thermal expansion of the bodies so that typical semivitreous dinnerware glazes are placed under adequate compression.

These low-temperature vitreous or near-vitreous bodies would seem to be primarily adaptable for single-fire ware. For producing flatware, it will be necessary to develop glazes which have abrasion- and corrosion-resistance properties equal to those of the present dinnerware glazes at four or five cones lower than the temperature at which the body matures.

Acknowledgment

The author wishes to express his appreciation to G. A. Bole for his helpful suggestions and to A. E. Baggs for his kind cooperation. This study was sponsored by the American Nepheline Corp., Rochester, N. Y., the Great Lakes Foundry Sand Co., Detroit, Mich., and the Edgar Plastic Kaolin Co., Metuchen, N. J.

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COMMERCIAL FIRING SURVEY OF CAR-TUNNEL KILNS*

By McDonald S. Nelson and Hewitt Wilson†

Abstract

Firing data were received from forty-eight manufacturers of many types of ceramic products. The products were divided into six classes, and minimum, maximum, and average values are presented in chart form on the firing cycle, loading, heat consumption, and firing costs. Fuel costs are analyzed, and data are given for two small, electric, twin-tunnel kilns.

I. Introduction

In connection with the study of electric firing of ceramic products, which is a continuation of the tests originating with the Tennessee Valley Authority, the Electrotechnical Laboratory surveyed commercial ceramic firing practice. The survey included the loading, heat consumption, firing time, and uniformity of heating. It was thought that these data would be valuable in predicting the conditions and the products for which electric firing might be considered feasible.

Data were received from forty-eight manufacturers in all parts of the country, covering the operation of sixty-one kilns producing nearly all types of ceramic products. A given manufacturer can use the classified data for comparing his own operation with the maximum, minimum, and average figures in his particular field.

II. Product Classification

To obtain comparable figures, the products were divided into six general divisions as follows: (1) glost firing of pottery and wall tile, (2) building brick and tile, sewer pipe, and terra cotta, (3) electrical porcelain, spark plugs, and other specialties, (4) clay and aluminous firebrick and shapes, (5) bisque dinnerware, tableware, stoneware, and artware, and (6) sanitary ware. Table I shows the different products and the number of kilns included in each class as reported by the manufacturers.

Differences in kiln size, loading technique, and firing cycle introduced wide variations in many instances. The classification of Table I, therefore, would group the products and data in a general way in relation to the type of loading, firing cycle, and maturing temperature.

III. Calculations

Table II shows the method of calculations using data from the Laboratory electric, twin-tunnel, walking-beam kiln as an example, the calculations being made for firing commercial face brick. The calculations involved in Nos. 15 through 25 in Table II are shown in parentheses.

After the individual kiln data were calculated, the results were grouped according to product classification. Minimum, maximum, and average values were determined for firing cycle, loading, loading space, heat consumption, and firing costs.

IV. Results

A compilation of the data is presented in Figs. 1, 2, and 3. In all instances, minimum values are shown by the black section, average values, by the black plus the cross-hatched section, and maximum values, by the total column. The product classifications are arranged to give ascending or descending order of the average values.

(1) Loading and Firing Cycle

Figure 1 shows the gross and net loading in pounds per cubic foot, the firing cycle in hours, and the setting space per hour in cubic feet. The loading and firing values depend on the type of ware being fired, whereas the setting space depends on the firing cycle as well as the size of the kiln. Building brick, tile, and firebrick showed the highest gross and net loads, and the bulky sanitary ware was lowest. Glost ware was fired on the fastest cycle, sanitary ware was third, and building brick and firebrick were fifth and sixth, respectively. Although all sizes of kilns were included, no great difference in averages among classes occurred in cubic feet

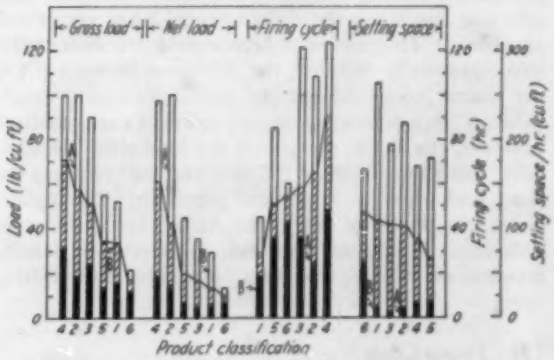

FIG. 1.—Gross and net loading (lb. per cu. ft.), firing cycle (hr.), and setting space per hour (cu. ft.); types of materials: 1, glost; 2, brick and tile; 3, electrical porcelain; 4, firebrick; 5, bisque; 6, sanitary ware.

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* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (Materials and Equipment Division). Received February 20, 1942.

† The authors are, respectively, assistant electrothermal engineer and supervising engineer, Electrotechnical Laboratory, Bureau of Mines, U. S. Dept. of Interior, Norris, Tenn. This paper is published by permission of the Director of the Bureau of Mines, and the work has been done in cooperation with the Tennessee Valley Authority.

TABLE I

TYPES OF PRODUCTS WITHIN CLASSES

Class 1 (glost)		Class 2		Class 3		Class 4		Class 5 (bisque)		Class 6	
Semiporcelain	2	Tile	6	Electrical porcelain	8	Refractories	6	Dinnerware	4	Sanitary ware, bisque and single fire	4
Hotel china	1	Brick	5	Spark plugs	1	Special refractories	1	Pottery tile	1		
Tile	3	Brick and tile	1	Special porcelain	2		7	Bathroom accessories	1		4
Dinnerware	4	Terra cotta	1					Stoneware	1		
Art pottery	1	Sewer pipe	1					Flowerpots	1		
	11		14		11			Vitrified china	2		
								Semivitreous ware	3		
								Vitreous artware	1		
									14		

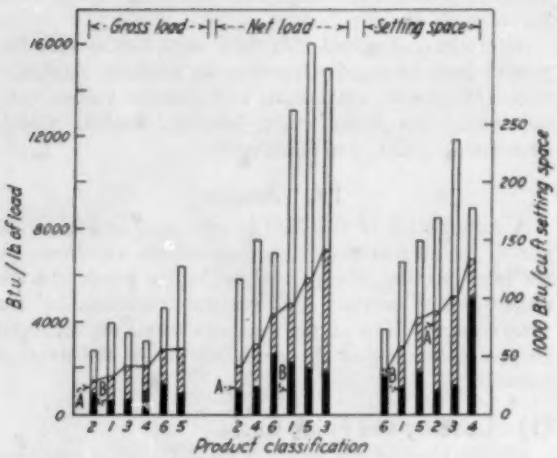

FIG. 2.—Consumption of B.t.u. per pound of gross and net loads and per cubic foot setting space.

per hour setting space. It is interesting to note, however, that the range of individual kilns was approximately 8 to 265 cu. ft. per hr.

(2) Heat Consumption

Figure 2 shows the B.t.u. consumption per pound of gross and net loads and per cubic foot setting space. A probable balance among ware, kiln furniture, and schedule minimizes the differences in B.t.u. per pound gross load. In the case of heavy products where little kiln furniture is required, the difference between B.t.u. per pound gross load and per pound net load is small. When a large number of saggers and decks are required, however, the B.t.u. per pound net load rises considerably; for example, class 2 (brick and tile) requires the least and class 3 (electrical porcelain) the highest B.t.u. per pound of net load. As in Fig. 1, the great differences in kiln size and firing cycle prevent definite conclusions relating to B.t.u. per cubic foot setting space.

(3) Firing Costs

Figure 3 shows the relative fuel costs of firing, which is probably of the most interest to the manufacturer. The fuel cost depends principally on the type of product

TABLE II

DATA AND CALCULATIONS ON FIRING COMMERCIAL FACE BRICK

1	Type of kiln:	Electric twin tunnel
2	Type of ware fired and product classification:	Brick, class 2
3	Pyrometer temp. (°F., cones):	2048°F., 4[d]
4	Cone variations (min. to max.):	1/6 cone
5	Schedule and length:	26 hr., 55 ft.
6	Fuel used:	Electricity
7	Cost of fuel per unit:	6 mills
8	Calorific value of fuel:	3415 B.t.u.
9	Fuel consumption per hour:	89.2 kw.-hr.
10	Cost per 10[6] B.t.u.:	1759 mills
11*	Gross load per cu. ft.:	66 lb.
12	Net load per cu. ft.:	66 lb.
13	Movement of load per hr.:	2 ft.
14	Setting cross section:	2 sq. ft.
15*	Setting space per hr. (13 x 14):	4 cu. ft.
16	Gross load per hr. (11 x 15):	264 lb.
17	Net load per hr. (12 x 15):	264 lb.
18	Heat used per hr. (8 x 9):	304,300 B.t.u.
19	" " " lb. gross load (18/16):	1152 B.t.u.
20	Heat per lb. net load (18/17):	1152 B.t.u.
21	" " " cu. ft. setting space (18/15):	76,070 B.t.u.
22	Cost per hr. (7 x 9):	535 mills
23	" " lb. gross load (22/16):	2.03 mills
24	" " " net load (22/17):	2.03 mills
25	" " cu. ft. setting space (22/15):	134 mills

* Setting space and volumes are those above the car deck or above the slab in walking-beam or slab-push kilns; loads do not include any portion of car below deck surface or slab in electric kilns.

fired, the fuel used, and its unit cost, which shows a wide range in different parts of the country.

As in the case of B.t.u. per pound gross load, the differences in cost of firing per pound gross load for different products are reduced somewhat by variations in kiln furniture and schedules. Great differences, however, are noted in the cost of firing per pound net load. Heavy products, such as brick and tile, are fired for an average of about 0.5 mill per lb.; electrical porcelain has an average firing cost of 2.7 mills per lb. and, in one instance, of almost 6 mills.

(4) Fuel Costs

Table III gives an analysis of the unit fuel costs of the forty-eight plants included in the survey. The extreme variation in the cost of gas and oil is interesting, showing wide differences in cost of fuel in various parts of the country.

A breakdown of the fuels used for each of the product classifications is given in Table IV. Although the average cost of coal per million B.t.u. is 50% of the cost of gas and 39% that of oil, only five plants of forty-eight, or five continuous kilns out of the sixty-one covered in the survey, use coal. Of these five plants, two manufacture producer gas, that is, they fire indirectly with coal and directly with gas.

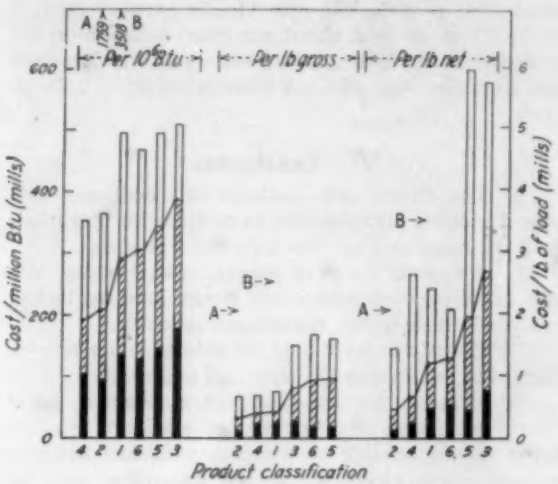

FIG. 3—Relative fuel costs of firing.

TABLE III

ANALYSIS OF FUEL COSTS

	Gas*		Oil		Coal	
	Cost/M (cents)	Cost/10⁶ (B.t.u., mills)	Cost/gal. (cents)	Cost/10⁶ (B.t.u., mills)	Cost/ton (dollars)	Cost/10⁶ (B.t.u., mills)
Min	10.0	95	2.14	151	2.75	102
Max.	50.0	476	7.10	506	5.12	185
Avg.	29.6	283	5.14	365	3.88	141
Plants (avg.)	28		15		5	

* Unavailable in many places.

TABLE IV

FUEL USED BY CLASSES

Class	Gas	Oil	Coal	Producer gas*	Total
(1) Glost pottery	9	2	0	0	11
(2) Brick and tile	9	2	2	1	14
(3) Electrical porcelain	5	5	1	0	11
(4) Firebrick	4	2	0	1	7
(5) Bisque pottery	9	5	0	0	14
(6) Sanitary ware	1	3	0	0	4
Kilns (total)	37	19	3	2	61

* From coal.

(5) Uniformity of Firing

Reports of temperature variation were received on forty-five of the sixty-one kilns. A variation range of 1/8 to 9 cones indicated the nonuniformity in cone temperature.

No. of cones	No. of kilns
1 or less	22
1 to 2	16
2 to 3	4
Above 3	3
Total	45

Of the twenty-two kilns showing 1 cone or less variation, fifteen were small, indicating that better uniformity is usually obtained with kilns of small cross section in which the heat penetrates easily to the middle of the load.

V. Application of Survey to Electric Firing

On a straight B.t.u. basis, electricity is much more expensive than gas, oil, or coal. Even in such regions as the Bonneville district where electricity can be obtained for 2 mills, a manufacturer could pay as high as 8.4 cents per gallon for oil, 58 cents per 1000 cu. ft. for 1000 B.t.u. gas, or $16.25 per ton for coal to equal the B.t.u. cost of electricity.* Because no commercial, electrically fired kilns are being operated in this country at bisque temperatures, no direct comparison of electric versus fuel firing is possible. The nearest approach to commercial bisque firing was conducted in the Tennessee Valley Authority electric, twin-tunnel kiln,[1] which is 55 ft. long and has a loading cross section of 1 sq. ft. per tunnel. The reduced length, cross section, and schedules of small kilns prevent direct and accurate comparisons with the large commercial kilns. Table V, however, shows comparisons among the Laboratory electric kiln, a commercial electric kiln firing at glost temperatures, and the three smallest commercial, fuel-fired kilns included in the survey. Glost

* The efficiency of combustion firing has been roughly estimated at 60% that of electric firing; on this assumption, the figures become 5.1 cents, 35.0 cents, and $9.80.

[1] (*a*) R. E. Gould, M. G. Toole, and M. S. Nelson, "Electric Kilns and Furnaces, V," *Jour. Amer. Ceram. Soc.*, 22 [7] 220–37 (1939).

(*b*) M. G. Toole and M. S. Nelson, "Heat Balance on Pilot Kiln, VI," *ibid.*, pp. 238–39.

TABLE V

COMPARISON OF SMALL ELECTRIC AND FUEL-FIRED KILNS

Fuel	Length (ft.)	Firing cycle (hr.)	Setting space /hr.(cu. ft.)	Firing temp. (°F.)	Gross load		Rating (%)
					Lb./hr.	B.t.u./lb.	
Electricity	55	26.0	4.0	2048	264	1152	100.0
"	65	12.3	9.5	1900	302	655	176.0
Gas	63	18.0	7.9	2000	402	2054	56.2
Oil	65	36.0	5.5	2318	420	3112	37.0
Gas	65	24.0	12.0	1860	409	3840	30.1

tile, pottery, electrical porcelain, and face brick were fired in these kilns.

Taking the reciprocal of the B.t.u. per pound gross load of the Laboratory electric kiln as 100% rating, the three fuel-fired kilns are shown to have ratings of 56 to 30%, although one operates at a lower temperature and one on a faster schedule and all have a greater gross load per hour. The efficiency of the Laboratory electric kiln may be considerably improved by better insulation and increase in length.

The individual data of the two electric kilns in Table V are given by arrows *A* and *B* in Figs. 1, 2, and 3; *A* is the Laboratory twin-tunnel kiln, and *B* is a commercial electric kiln operating at glost temperatures. In comparing kiln *A*, used for firing face brick, with the averages of class 2 (brick and tile), it should be kept in mind that these averages include kilns having a production fifty to sixty times that of the electric kiln. The B.t.u. per pound of load for the electric kiln, however, is considerably lower than the average for class 2, and only four of the fourteen kilns included in this class show a lower B.t.u. consumption per pound of gross load. These data indicate that in regions where electricity is cheap, an efficiently designed, commercial-size, electric kiln[2] could compete with fuel-fired kilns even for firing brick and tile.

Face brick were obtained from two local manufacturers for the firing tests in the electric kiln. Brick that were equal in every respect to those of the manufacturer in one case were obtained in an 18-hr. firing cycle as compared to 102 hr. in the commercial tunnel kiln. Commercial-quality brick, in the second case, were obtained in 26 hr. as compared to the manufacturers' 7-day cycle in periodic downdraft kilns.

A variation of less than one-sixth cone was found in the 12- by 12-in. loading section of the kiln on a 26-hr. schedule. Tests for uniformity of firing conducted in an electric, periodic kiln with a loading cross section of 16 by 21 in. showed about one cone variation on the equivalent of a 24-hr., tunnel-kiln cycle and less than one-sixth cone variation on the equivalent of a 48-hr. cycle.

VI. Conclusions

(1) The charts and methods of calculation presented enable a manufacturer to compare his operations with the range and average for similar products.

(2) The wide range of energy, cost, loading, kiln size, and firing cycle within unit groups indicates lack of standardization within the ceramic industry.

(3) Electric firing should be able to compete with fuel firing on a basis of quality and uniformity.

(4) Because of its more direct application, lower heat losses, and resulting higher efficiency, electric firing should be able to compete with fuel firing in regions where electricity is not expensive, such as the Pacific Northwest, parts of the Pacific Southwest, and the Tennessee Valley.

Acknowledgment

The authors wish to thank the forty-eight manufacturers whose cooperation and complete data made this survey possible.

Electrotechnical Laboratory
U. S. Bureau of Mines
Norris, Tennessee

[2] M. S. Nelson and Hewitt Wilson, "Multiple-Tunnel Kilns," *Bull. Amer. Ceram. Soc.*, **20** [8] 270–74 (1941).

ANOTHER PUBLICATION ISSUANCE SCHEDULE

The postal authorities will not permit the issuance schedule for the *Journal*, *Ceramic Abstracts*, and *The Bulletin* as inaugurated with the February issues of 1942 and continued through the April issue.

To meet the objections, (1) *The Journal*, beginning with the May issue, will go into the mail on the 1st of the month; its present volume is Vol. 25. (2) *Ceramic Abstracts* and *The Bulletin* will be issued under one cover on the 15th of the month; the current volume number of each publication is Vol. 21.

These two changes made in the midyear publication should not confuse any binder if a careful check is kept on consecutive page numbers.

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